Investigation of Nitrogen Compound Types in High-Boiling Petroleum Distillates from Saudi Arabian Crude Oils

by

Mohammed Ashraf Ali

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
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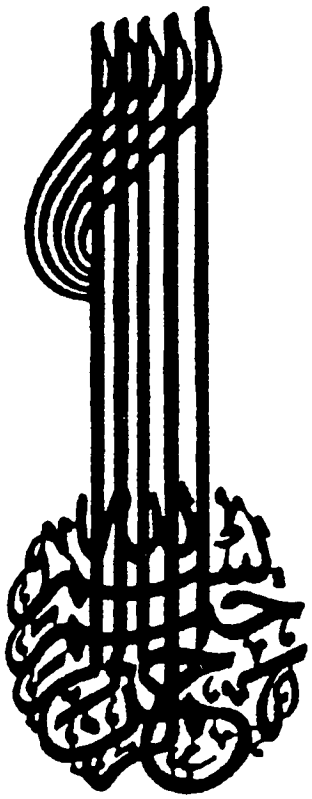

KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS

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This thesis, written by Mohammed Ashraf Ali Shaikh under the direction of his Thesis Committee, and approved by all its members, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfilment of the requirements for the degree of Master of Science in Chemistry.

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DEAN, COLLEGE OF GRADUATE STUDIES

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This Thesis is Dedicated to
my Brothers and Sisters and
to the Memory of my Parents

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الخلاصـــــــــــة

تهدف هذه الدراسة الى فصل الأحماض والقلويات ومركبات النتروجيـــــــــن المتعادلة فى مقطرات التقطير العالي (٣٧٠°م - ٥٣٥°م) للخام العربي السعـــــودى الثقيل والمتوســـــط .

تم العمل التمهيدى على أنواع الخام العربي السعودى الأربعة ومقطراتهـــا فى المدى (٣٧٠°م - ٣٥°م) حيث حضرت المقطرات تحت الضغط الجوى العادى وتحـــــت الضغط المتخفـــــض .

أظهرت الدراسة ان القلوية والعطرية ومتوسط الوزن الجزيئي ودرجة تعـــدد الحلقة تزداد مع زيادة المحتويات متغايرة الذرات وبقايا الكربون ولزوجـــــة المـــــادة .

تم فصل الأحماض والقلويات بواسطة مبادل أنيوني وكاتيوني راتنجـــــــــي بالترتيب بينما أزيلت مركبات النتروجين باتحادها مع كلوريد الحديديك المحمـل على طفل أتا بالجـــــس .

كما تم فصل هذه المقطرات فيما بعد الى مركبات نتروجين مميزه هـــــــي بيريدينات وبيرولات وأمايدات باستعمال سائل تحليل كروماتوجرافي عالـــــــــي الأداء على ألومنيامتعادلـــــــة .

وقد طورت طريقة المعالجة اللامائية لفـرق الجهد لتعيين النتروجيـــــــن القاعدى والغير قاعدى فى المقطرات المفصولة وقادت معالجة المقطرات والمنتجات الى تعيين النتروجين القاعدى القوى والضعيـــــف .

واستخدم التحليل بالأشعة تحت الحمراء لتعيين معظم كمية الاصناف وقورنـــت النتائج مع نتائج المعالجة والنتروجين الكلي واظهرت المقارنة بين الطريقتيـن الى أنه يمكن استعمال هذه التقنية لتعيين انواع مركبات النتروجين على أســـاس التحليل الطيفى بالأشعة تحت الحمراء وفوق البنفسجية ، كما استخدم الضغـــــط البخارى الأوزومترى لتعيين متوسط الوزن الجزيئي وتم تصنيف مركبات النتروجيـــن المستقلة باستعمال محلل الغازات - مطياف الكتلة وثم التعرف على ستة عشـــــر مركبا من مركبات النتروجين بواسطة محلل الغازات - مطياف الكتلة والتى اعطيت ثلاثة أنواع وهي البريدين والبيرول والأمايـــد .

ABSTRACT

This study aims at the selective separation of acids, bases and neutral nitrogen compounds from high-boiling distillates (370-535°C) of Arab Heavy and Arab Medium crude oils. Preliminary work was carried on all four Saudi Arabian crude oils and their distillates in the boiling range 370-535°C(700-1000°F). The distillates were prepared using atmospheric and vacuum distillation. The study has shown that the basicity, aromaticity, average molecular weights and degree of ring condensation in distillates increase with an increase in heteroatomic contents, carbon residues and viscosity of the material. Acids and bases were separated with anion and cation exchange resins respectively while the neutral nitrogen compounds were removed by complexation with ferric chloride supported on Attapulgus clay. These fractions were further separated into distinct nitrogen compound types namely pyridines, pyrroles and amides using high performance liquid chromatography on neutral alumina. A nonaqueous potentiometric titration method was developed to determine the basic and nonbasic nitrogen in the distillates and the separated fractions. Titration of distillates and HPLC fractions also led to the determination of strong and weak basic nitrogen. A chromatographic-Infrared method was used for the quantitative determination of major compound types. The results were compared with titration and total nitrogen data. Comparison of the results from the two methods has shown that these techniques can be employed for the determination of compound types in complex petroleum fractions. Characterization of nitrogen compound types was made on the basis of infrared and ultraviolet spectroscopy. Vapor pressure

osmometry was used to determine the average molecular weights. Characterization of individual nitrogen compounds was accomplished using gas chromatography and gas chromatography-mass spectrometric analysis. Sixteen nitrogen compounds were positively identified by GC-MS analysis. These compounds represent three compound types which are pyridine, pyrrole and amide.

CHAPTER 1

INTRODUCTION

1.1 GENERAL INTRODUCTION

The upgrading of high-boiling distillates and residue to light petroleum products such as gasoline, diesel fuels and chemicals is becoming an extremely important subject for research and development. This is because of decreasing availability of light petroleum and increasing energy requirements. Increased energy requirements together with increased environmental constraints require more efficient use of the high-boiling distillates and residues. The present trend and probably long term future prospects for hydrocarbon conversion industry is to utilize the heavier feedstocks. Such feedstocks are characteristically more difficult to process due to higher aromaticity, increased heteroatomic contents, metals and high molecular weight as compared with light petroleum. Moreover, during processing of crude oils, these heteroatomic compounds get concentrated in the heavy ends, causing additional difficulties. These factors will require increased processing, which to be efficiently accomplished, require a more intimate knowledge of the composition of high-boiling distillates and residues in terms of heteroatomic compounds present.

The characterization of nitrogen compounds in the high-boiling distillates is done differently than in the low boiling fractions. In the low boiling fractions, individual compounds can be isolated and characterized. As the boiling point increases, the structural diversity of the hydrocarbon increases and many families of heteroatomic

compounds become important constituents. Therefore, separation and analysis must be done by compound types rather than by individual compounds.

There are many separation schemes reported in the literature. Generally, in all of these schemes, crude oil distillates are separated into various polar, nonpolar and hydrocarbon fractions by column chromatography or high performance liquid chromatography. A simplified scheme (1), originally developed by the joint efforts of Bureau of Mines and American Petroleum Institute permits classification of heavy ends of crude oils into seven fractions viz acids, bases, neutral nitrogen compounds, saturates, monoaromatics, diaromatics and polyaromatics. Further identification of these fractions is done to identify the major compound types present. Recent research by numerous investigators have utilized various separation methods and analytical instrumentation techniques for the identification of nitrogen compounds in petroleum and shale oils. The work done by these researchers is thoroughly reviewed in the next chapter.

Separation methods applied to isolate nitrogen compound types in our work included ion-exchange chromatography, coordination complexation chromatography and high performance liquid chromatography. Characterization techniques applied to the nitrogen compound types included infrared spectroscopy, ultraviolet spectroscopy and nonaqueous potentiometric titration. Characterization of individual compounds was achieved using gas chromatography and gas chromatography-mass spectrometry.

1.2 NEED FOR THE STUDY

Nitrogen compounds are an important constituents of petroleum and related materials. Even in trace amount, they cause serious problems in processing and in the stability of the products. Environmentally and from the process point of view, the presence of nitrogen compounds in petroleum is undesireable. Following are the deleterious effects of nitrogen compounds

(1) Nitrogen compounds present in crude oils are responsible for the deactivation and poisoning of catalysts employed in cracking, hydrocracking, reforming, hydrodesulfurization and hydroprocessing. The investigations (2) carried out in this field have shown that this is a vital problem and its solution is important for petroleum industry. In case of basic nitrogen compounds, the damaging effects are thought to arise from basic nitrogen neutralizing the active catalytic sites which are acidic in nature. Basic nitrogen compounds are among the worst offenders in promoting high carbon deposits on cracking catalysts (3). Nitrogen compounds are present in various chemical forms and it is important to know the type and amount of these species. In processing, the character and content of nitrogen compounds must be known in order to choose the appropriate catalysts and conditions for their removal during refining. Investigators have also reported that catalytic removal of nitrogen compounds from petroleum and shale oils is much more difficult than sulfur removal(4,5). This difficulty in removing nitrogen compounds probably reflects the refractory nature of the cyclic nitrogen compounds which contain major portion of nitrogen present in petroleum and shale oils. This factor further stress the need of

characterization of nitrogen compounds present in petroleum.

(2) Formation of gums, lacquers and sediments have been observed during storage of fuels and oils derived from petroleum. It is known that nitrogen compounds effect jet fuels stability upon storage. The higher the nitrogen contents of a fuel, the poorer its storage stability. The problem is becoming more worse because of increased use of lower grade petroleum which is higher in nitrogen contents. Jet fuels may be considered as hydrocarbon fuels because their heteroatomic contents amount to only a few tenths of a percent. However, the trace impurities exert significant deleterious effects on the stability of the liquid fuels by promoting sediment formation. It has been observed that precipitates obtained from various fuels are much higher in nitrogen than the parent oils (6). This proves that sediment formation is due, in large, to the nitrogen containing species. Nixon (7) states that while certain nitrogen bases are deleterious, others are not. Aniline may exert a beneficial effect while pyrroles are markedly deleterious. Other compounds present in the fuel especially unsaturated hydrocarbons, may interact with nitrogen containing compounds to form sediments. Thus, according to Nixon, the most unstable fuels are those containing thermally and/or catalytically cracked base stocks (high in unsaturates) in combination with a high nitrogen contents. This observation is also supported by other investigators (8,9,10). These workers reported interaction between 2,5-dimethylpyrrol (DMP) and olefins under high temperature and at room temperature storage. The combination of olefins and nitrogen compounds may also inhibit the action of antioxidants in fuels (11). Some Russian workers have

demonstrated the beneficial effects of removing nitrogen bases from jet fuels (12,13). A three-fold reduction in oxidation and nearly a ten-fold reduction in gum formation was observed in removing the nitrogen from test materials in one of the experiment. Thompson, et al. (6) and Dinneen and Bickel (8) regarded both pyrroles and pyridines compounds as promoters of sludge formation in fuel oils. On the other hand, other workers (14,15,16) have found that some nitrogen bases have little or no effect on fuel stability. In fact, enhanced stability has been claimed for fuels containing pyridines. In general, nitrogen compounds contribute to instability of petroleum derived fuels. Investigations (10) have shown that nitrogen compounds promote sediment formation in jet fuels stored under ambient conditions. It was found that the three compounds giving the highest amount of sediment are of the pyrrole types namely DMP, Indole and carbazole. Among other compounds studied, only 2,6-dimethyl aniline and 2-methylpiperidine afforded any measurable sediments. In another study (17), the average molecular composition and the proposed structure of the sediment samples suggest that DMP plays a major role in sediment formation. Studies have also shown that sediment formation increases with increasing DMP concentration, storage time and with increasing temperature of the fuel(18). A study conducted by Loeffler (19) has shown that DMP has greater tendency towards sediment formation than DMQ (dimethylquinoline) and sedimentation is enhanced in the presence of sulphur containing compounds. This study also proves that nitrogen compounds are deleterious to the storage stability of the fuels and oils.

(3) Nitrogen compounds are also known to adversly effect the color stability of various petroleum products which lead to change in color of a fuel. It has been reported several of the primary amines decolorise petroleum and their products and the color is intensified with time.

(4) Nitrogen polyaromatic compounds found in petroleum present environmental and occupational health hazard because of their toxicity. Wynder and Mabuchi (20) estimated that 70-90 percent of human and animal cancer is caused by environmental factors. Among the environmental toxic chemicals concerned, nitrogen polyaromatic compounds comprises the second largest group of carcinogenics after polyaromatic hydrocarbons. Nitrogen polyaromatic compounds are widely spread in our environment, primarily due to their escape from combustion processes. A number of nitrogen polyaromatic compounds, range from two to five membered rings, have been identified in air particulate matter (21). Different amounts of nitrogen polyaromatic compounds in the urban atmosphere of several major American cities were reported by Sawicki et al. (22). Nitrogen polyaromatic compounds have been tested for their toxicity, since these compounds are known to be present in the atmosphere. In a biological study (23) conducted on the nitrogen polyaromatic compounds, it was found that among neutral nitrogen compounds, 7H-dibenzo[c,g]carbazole is a highly potent carcinogen and 13H-dibenzo[a,i]carbazole a suspected carcinogen. Following this and other observations (24) that some dibenzocarbazoles and dibenzoacridines are active, detailed studies on nitrogen polyaromatic compounds and their biological activities were carried out (25). These authors claim that carcinogenicity of some of these

compounds may be greater than that of 3-methylbenz[j]aceanthrylene, a very potent carcinogen. Within the series of benzacridines, high activity was encountered with the angular types(e.g. benz[a]acridines and benz[c]acridines) as opposed to the linear benzacridines. Among the large number of alkylated benzacridines tested for carcinogenicity, the benz[c]acridines possess greater toxicity than the benz[a]acridines. It has been reported that there is a correlation between pKb values of such compounds and their carcinogenic activities. A large number of other heterocyclic polyaromatic compounds have been tested more recently, including diaza compounds and nitrogen polyaromatic compounds containing sulphur or oxygen. Carcinogenicity of these nitrogen compounds (26)· also provoke some concern over the development of certain methods for their detection in various materials to which humans are frequently exposed.

(5) Certain nitrogen compounds together with associated polar compounds are also known to cause the oils and bitumens to adhere strongly to the sand, clay and rock surfaces of the reservoir which adversly effect secondary and tertiary recovery of oils.

(6) Fuels derived from petroleum are usually high boiling distillates and residue which are high in nitrogen contents. When these fuels are burnt for heating and lighting purposes, they produce toxic combustion products such as Nitrogen oxides which are environmentally hazardous.

Consequently, the characterization of the nitrogen compounds is of very importance. It is needed because nitrogen compounds are present in very low amount in most of the crude oils. This is also needed

because all classes of nitrogen compounds are not deleterious. e.g. pyrrolic types, in particular, and some amines have been observed deleterious while some other types not. The challenge is further enhanced by our restricted knowledge of the origin and geochemical cycles of fossils containing nitrogen.

CHAPTER 2

LITERATURE REVIEW

2.1 NITROGEN CONTENTS OF PETROLEUM

The total nitrogen contents of petroleum is low and generally falls in the range of 0.1-0.9 percent. Early work indicated that some crudes may contain nitrogen up to 2 percent. However, crude oils with trace amounts of nitrogen are not uncommon. In general, the more asphaltic the oil, the higher its nitrogen contents. On the other hand, the greater paraffinicity of an oil results in low nitrogen content.

A study of the world crude oils (27) shows that there exists a correlation between API gravity and nitrogen content of these oils. It follows that as API gravity of an oil increases, the crude becomes lighter and this results in low nitrogen content. It also leads to an approximate relationship between carbon residue and nitrogen contents of most of the crude oils of the world. The higher the carbon residue, the higher will be the nitrogen content of that oil. Thus nitrogen and other heteroatoms are heavily concentrated in high-boiling fractions of crude oils.

2.2 NITROGEN COMPOUNDS FOUND IN PETROLEUM

Nitrogen present in crude oil is found in a variety of different compounds ranging from aliphatic amines to polycyclic nitrogen compounds. It also occurs to a lesser extent in highly complex compounds such as porphyrins (28) which are nitrogen-metal complexes. These nitrogen compounds distribute themselves throughout the boiling

ranges of crude oil. However, this distribution is not uniform in that nitrogen compounds and their contents increases with increasing boiling point of petroleum fractions (29,30,31). Lower boiling compounds such as aniline and alkylamines are aliphatic in structure and are present in the lower boiling fractions. On the other hand, heterocyclic nitrogen compounds have tendency to concentrate in the medium to high-boiling fractions and residues. Studies have shown that high-boiling petroleum fractions also contain heterocyclics with more than one nitrogen atoms such as azaindoles and azacarbazoles (30,31). Nitrogen compounds with sulfur and oxygen atoms (31) have also been characterized.

Nitrogen compounds in petroleum may be classified as basic and nonbasic. The basic compounds which mainly consist of pyridine, quinoline and acridine types occur throughout the boiling ranges, but have a decided tendency to exists in the high-boiling fractions. The nonbasic nitrogen compounds which are usually of the pyrrole, indole and carbazole types also occur in the high-boiling fractions and residues.

The following generalizations can be made about the basicity of nitrogen compounds.

1. Basicity decreases from aliphatic to aromatic nitrogen compounds (compare pentylamine and pyridine).
2. Among various types of nitrogen compounds, the trend of basicity is

   Pyridines > Amides > Pyrroles

3. A fused aromatic ring decreases the basicity of the nitrogen

compounds (compare imidazole and benzimidazole).

4. A second heteroatom in the ring containing a nitrogen atom decreases the basicity of the compound significantly (compare pyridine and pyrazine).
5. Electron withdrawing groups on the ring such as hydroxyl(OH), cyano(CN) and chloro(Cl) decrease the basicity of the compounds (compare cyanopyridine and pyridine).
6. Electron donating groups such as alkyl substituents increase the basicity of the compounds (compare methylquinoline and quinoline).
7. Saturation of the ring converts a nitrogen compound to a much stronger base (compare pyridine and piperidine)

2.3 ISOLATION OF NITROGEN COMPOUNDS FROM PETROLEUM AND RELATED MATERIALS

The complexity of petroleum increases rapidly with increasing boiling point of the fractions not only because of the increase in the number of possible isomers of any given carbon number, but also because of the prevalence of heteroatomic compounds. In the presence of these heteroatomic compounds, the usual separation and isolation schemes known to work for purely hydrocarbon mixtures should not be expected to be applicable and usually are not.

It has been recognized that compositional analysis of high-boiling petroleum fractions by the isolation of individual compounds is a practical impossibility (32). Instead, many attempts have been made to separate these complex mixtures into classes of compounds or compound

types. Identification of nitrogen compound types in high-boiling distillates require extensive separation of the starting material. Numerous separation methods and schemes have been developed in the past for the analysis of heteroatomic compounds in petroleum and related materials (33,34,35). Most of these techniques are based on different forms of chromatography such as ion-exchange chromatography, adsorption chromatography, paper chromatography, gas chromatography, high performance liquid chromatography, reverse phase liquid chromatography, acid extraction, complexation and coordination chromatography and liquid thermal diffusion (36). All of these separation methods require precautionary measures to protect heteroatomic compounds from compositional changes. One of the systematic studies on composition of high-boiling distillates and residues was the API research project 60 and latter work based on the characterization schemes developed under the project (37-47).

There are several studies regarding the acid extraction of nitrogen compounds from petroleum and related materials.

Hartung and Jewell (48) used aqueous hydrochloric acid extraction for the separation of basic nitrogen compounds from petroleum fractions. Many nitrogen compounds were separated and characterized in this study.

Drushell and Sommers (49) employed perchloric acid extraction along with aqueous hydrochloric acid for the separation of basic nitrogen compounds. This method also separated very weak basic nitrogen compounds such as pyrroles and carbazoles.

Khan and co-workers (50) employed a method based on extraction. They performed extraction of basic nitrogen compounds from high-boiling petroleum distillates using different concentration of aqueous sulfuric acid. This scheme separated nitrogen compounds into two portions. Some nitrogen compounds were soluble in aqueous acidic media while the others were separated as dark brown gummy nitrogenous material.

Burchill et al. (51,52) have reported separation of aza-arenes (alkyl homologs and benzologs of pyridines and pyrroles) and aromatic amines in coal tar by a procedure involving acid extraction followed by GC-MS analysis.

Das et al. (53) have reported extraction of nitrogen bases from Indian coal tar. The method involved acid extraction, fractionation, derivatization and analysis by GC-MS. Extraction was performed repeatedly with 10 and 20 percent solution of sulfuric acid. Fractionation based on polarity was necessary, since a packed column was used in place of a capillary column for GC-MS separation and characterization. Derivatization was utilized to distinguish amines from aza-arenes.

Schmitter et al. (54,55) have developed a fast and reproducible method for the separation of nitrogen bases from petroleum. The method involved trapping of quaternary ammonium salts of basic nitrogen compounds on hydrochloric acid treated silica which were desorbed from the column using appropriate solvents. The separation was achieved in a chromatographic column packed with this adsorbent

and was provided with a solvent recycling system. The method allowed a selective and quantitative extraction of basic compounds from large amount of crude oil. The selectivity and reproduciblity of this method was tested with mixtures of model compounds representing the major classes of petroleum constituents. This method has been applied to fifteen different samples.

Beiko et al. (56) separated the nitrogen bases from low-boiling distillates of Dzharkurgan crude oil of south Uzbekistan. The method involved the concentration of nitrogen bases by acid extraction and separation on active alumina using a series of solvents. The fractions obtained were further analyzed by high speed liquid adsorption chromatography.

Tomkins and Ho (57) reported isolation of polycyclic aromatic amines in natural and synthetic crudes. The amines were isolated through an extensive acidic extraction and adsorption along with gel permeation chromatographic purification procedure. The amines were separated as trifluoroacetylated derivatives and identified by GC-MS. The method is useful for profiling amines in such diverse matrices such as petroleum, shale oil and coal-derived materials. This study showed that all polyaromatic amines in these materials may be separated, characterized and quantitated successfully.

Wallace and Crook (58) have employed the method of Schmitter et al. (55) to isolate the nitrogen bases from coal-derived asphaltenes and preasphaltenes using acid modified silica. The method offers a high degree of enrichment of nitrogen compounds.

Bianco et al. (59) have reported isolation of basic nitrogen compounds from coal-derived liquids using the method of Schmitter et al. (55). Basic nitrogen compounds were separated and part of it was derivatized with trifluoroacetic anhydride. Both derivatized and underivatized basic compounds were characterized.

While going through the literature, it soon became clear that liquid-liquid extraction methods work well only with low-boiling (<350°C) distillates. The main problems encountered during extraction were poor solubility of larger and more hydrophobic polar molecules in either an aqueous or an aqueous-alcoholic phase as evidenced by the emulsions formation, precipitation and poor recoveries observed. As a supporting evidence, Tomkins and Ho (57) found that 1-aminopyrene (molecular weight=217) was near the upper limit of extractable amino-polyaromatic hydrocarbons. McKay et al. (41) estimated the average molecular weight of nitrogen bases in 370-535°C petroleum distillates to be about 400. Hence, extraction techniques cannot be expected to work well with mid or high-boiling distillates and residues. Furthermore, extensive alkyl substitution often found in petroleum compounds further aggravates the hydrophobicity problem.

Dinnen and co-workers (60) separated many types of nitrogen compounds from Colorado shale oil. The nitrogen compounds were concentrated by Florisil adsorption and fractionated through vacuum distillation and thermal diffusion. The nitrogen compound types were identified by spectral studies.

Peters and Bendoraitis (61) employed Florisil adsorption

chromatography for the separation of polar compounds from petroleum. The method used a ratio of Florisil:oil (10:1) for the efficient separation of nitrogen and oxygen containing compounds. Many compounds were separated and characterized.

Al-Kashab and Neumann (62) performed direct separation of heteroatomic compounds from deasphalted residues on a dual alumina-silica column. These heteroatomic compounds were further separated into acidic, basic and neutral nitrogen compounds using anion and cation-exchange chromatography.

Drushell (63) separated heteroatomic compounds from maltenes through chromatography on clay-silica column. The method has good reproduciblity and can be applied to petroleum and related materials. Many nitrogen compounds were separated and characterized in this study.

Sawatzky and co-workers (64) reported two fast methods for the separation of heavy petroleum ends into hydrocarbons and polar material. These methods employed pressurized columns and have greatly reduced the time of analysis. One of the two methods is developed for the analysis of feedstocks in the refineries and pilot plants and it reduced the time of analysis by a factor of ten as compared to USBM-API method. The second method is specially developed for analysis of very small amount of samples and it is hundred times faster than USBM-API method. Both of these methods are based on adsorption chromatography on activated silica-alumina column using different solvent systems.

Schiller (65) employed neutral alumina (activity I) for the separation of nitrogen compounds from coal-derived liquids. A column packed with this adsorbent was used and a number of nitrogen compounds were separated from the samples using different solvents.

Working with coal liquefaction products, Farcasiu (66) observed irreversible adsorption of the more polar constituents of coal-derived liquids on activated alumina and loss or chemical changes in pyrrole type compounds on strong ion-exchange resins of the type used with the SARA method (67). Farcasiu (66) developed a fractionation scheme design to overcome the problem of coversion of certain nitrogen compound types during separation. This method allowed the fractionation and recovery of essentially the whole coal sample. This scheme is based on chromatographic fractionation of both benzene-soluble and pyridine-soluble components by sequential elution with specific solvents (SESC) on a silica gel column. The criteria used in choosing the sequence of the solvents for eluting the polar material are based on the Hildebrand parameters and specific solubility parameters.

Ford et al. (69) designed a method for the separation of nitrogen compounds from shale oil products by adsorption chromatography on basic and neutral alumina. The basic alumina separated the shale oil into four nitrogen-rich fractions. These fractions containing nitrogen compounds were further fractionated by neutral alumina using different solvent system for elution. The separation scheme was successfully applied to shale oil products which differ in boiling range and in total nitrogen contents. This scheme offered fast and reproducible results and separated the materials into pyridine, pyrrole and amide type

nitrogen compounds.

Holmes and Thompson (69) developed a scheme for the separation of nitrogen compounds by adsorption chromatography using alumina and silica. The nitrogen compounds were obtained in five fractions. The method can be applied to determine nitrogen compound distribution in crude shale oils, hydrotreated whole shale oils, residues and distillates successfully. Several classes of compounds were separated.

High performance liquid chromatography has been used by Amateis and Taylor (70) for the separation of basic nitrogen compounds from coal-derived products using microbore column which offer better separation of nitrogen compounds.

Green et al. (71) separated polar compounds from solvent refined coal (SRC) liquids by high performance liquid chromatography using silica.

Finseth et al. (72) carried out a study regarding the performance evaluation of hydrochloric acid extraction and ion-exchange chromatographic separation of nitrogen bases. These two methods were applied on similar type of samples and results were compared with respect to total nitrogen contents and the types of nitrogen compounds present in the separated materials. This study indicated that the base fractions separated by cation resins contained more nitrogen than the fractions separated by hydrochloric acid precipitation. Average molecular weight determination of these fractions showed that approximately one nitrogen atom per molecule was present in the case of cation resin separated fractions whereas less than one nitrogen atom per

molecule was observed for hydrochloric acid precipitated fractions. High-resolution mass spectrometry of these fractions showed that acid precipitation method is selective for the aromatic nitrogen bases and does not separate highly hydrogenated nitrogen bases present in coal-derived liquids. So it appear that hydrochloric acid precipitation method is not comparable to ion-exchange method and should not be employed especially for the separation of high molecular weight nitrogen bases which are normally present in high-boiling distillates and heavy residues of petroleum and related materials.

Munday and Eaves (73) were the first who reported use of ion-exchange resins for fuel fractionation in 1959. They employed cross-linked gel type resins, since that was all available at that time, although these were not well suited for nonaqueous media.

Webster et al. (74) used microreticular resins for the first time for the separation of polar materials from fuels. These resins were so effective in separation that only a year later, Snyder and Buell (46) published an elaborate scheme including microreticular resin-based separations.

Snyder and Buell (75) have developed an integrated scheme for the separation of nitrogen and oxygen compound types present in high-boiling petroleum distillates. Anion and cation chromatography were used in conjunction with adsorption chromatography on alumina, silica and charcoal. The resulting separations are experimentally convenient, reproducible, predictable and sample recoveries are satisfactory.

Oudin (76) used the principle of Snyder (75) of preseparation of a petroleum sample into a neutral and a polar cut with subsequent separation into narrower fractions.

Investigators at Laramie Energy Technology Centre (37-41,44,77-81) have applied ion-exchange chromatographic technique to a large number of fossil fuels including coal-derived liquids, shale oils and tar sands as well as petroleum. In fact, a major advantage of nonaqueous ion-exchange resins is its wide applicability to virtually all samples and all boiling ranges.

The SARA method developed by Jewell (67) is an extension of the USBM-API method and permits faster and more standardized separations. The method employs a single column containing anion and cation-exchange resins in the upper half and ferric chloride-attapulgus clay and anion-exchange resin in the lower half of the column. This method isolates acids, bases and neutral nitrogen compounds collectively from petroleum and related materials. The method is flexible, reproducible and applicable to a large variety of oil samples including tar sand, bitumens and coal-derived liquids.

Green et al. (82) have developed an improved separation method based on ion-exchange separation of liquid fossil fuels into acids, bases and neutral fractions. Improvement was made in the activation of resins, desorption of separated materials from the resins and in the elution of different solvents.

Strachan and Johns (83) reported a separation scheme that separated coal-derived liquids into discrete compound types using

various nonaqueous ion-exchange resins (in a particular sequence) combined with silica and alumina adsorption flash chromatography. In this scheme, fractions were obtained on a large scale which were subjected to further analysis. The method offer good reproduciblity and better recovery of the samples. Many nitrogen compounds were identified in this study.

Jewell and co-workers (1) developed a separation method that fractionated high-boiling petroleum distillates and residues into acid, bases, neutral nitrogen compounds and hydrocarbons. This was the research project established under the joint sponsorship of the United states Bureau of Mines (USBM) and the American Petroleum Institute (API) and was named USBM-API method afterward. The method combined ion-exchange chromatography and coordination chromatography with adsorption chromatography. The acid and base fractions were isolated by ion-exchange chromatography and the neutral nitrogen compounds were separated by coordination chromatography on ferric chloride-Attapulgus clay. This scheme has been applied to high-boiling petroleum distillates and residues from a variety of crude oils having different compositional characteristics. Among all the separation schemes discussed, this method, at present, is the most comprehensive and most widely applicable for the fractionation of petroleum and related oil samples into distinct fractions. Despite its disadvantages of tediousness, more time consuming and possible loss or coversion of polar and highly condensed compounds, the method can be viewed as the yardstick by which other faster methods should be measured. Several investigators have employed this method (37-41,84) or its modified form (85-87) to

separate nitrogen compounds from petroleum and related materials.

2.4 ANALYTICAL METHODS OF CHARACTERIZATION

Nitrogen compounds are present in petroleum in various chemical functionalities. It is important to know the type and amount of these compounds in order to choose the appropriate catalysts and conditions for their removal during refining.

Characterization of nitrogen compounds is reported in the literature using various analytical techniques which include elemental analysis, vapor pressure osmometry (VPO), infrared spectroscopy (IR), ultraviolet spectroscopy (UV), nonaqueous potentiometric titration (NAPT), gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), mass spectrometry (MS), fluorescence spectroscopy (88,89), phosphorescence spectroscopy (90) and nuclear magnetic resonance spectroscopy (NMR). Each of these methods provide specific structural and compositional information. The informations from these various sources when combined, can lead to a detailed picture of nitrogen compounds present in high-boiling distillates and residues.

2.4.1 ELEMENTAL ANALYSIS

The elemental composition of a petroleum sample can be used to derive its empirical formula which is very helpful in the characterization of the materials. Several methods have been employed for determining elemental composition of petroleum samples and related materials.

Dinnen and co-workers (60) employed Kjeldahl method for total nitrogen contents determination. Snyder et al. (29) used Kjeldahl method for the determination of total nitrogen contents and X-ray fluorescence technique for total sulfur determination in the distillates of a crude oil. McKay et al. (38) employed micro-Dumas method for the determination of total nitrogen contents of base fractions from different petroleum distillates and residues. McKay et al. (41) also employed macro Kjeldahl and microcoulometric (Dohrmann) method for nitrogen contents determination. Holmes and Thompson (69) employed chemiluminescence method for nitrogen content determination in shale oils.

2.4.2 MOLECULAR WEIGHT DETERMINATION

Molecular weight determination is very important for analyzing complex mixtures in order to know the average weight of the molecules present in the sample. This information together with elemental composition can lead to the characterization of the sample. Various techniques have been used to determine molecular weights of distillates and residues.

McKay et al. (38) employed four different techniques for average molecular weight determination of high-boiling distillates and residues. These techniques were vapor pressure osmometry, electron ionization mass spectrometry, field ionization mass spectrometry and quantitative infrared spectroscopy. The molecular weights used for the characterization of samples were the average of molecular weights determined by all four methods. Khan et al. (50,85) employed low

voltage mass spectrometry for average molecular weight determination.

Snyder and Buell (75) employed vapor pressure osmometry and mass spectrometry for average molecular weight determination of several petroleum fractions of a California crude oil.

2.4.3 INFRARED SPECTROSCOPY(IR)

Infrared spectroscopy has been used widely for the characterization of nitrogen compound types because most of these compounds have absorbance in the infrared region. The most commonly identified functional groups are pyridines, pyrroles and amides. Pyridine benzologs and their alkyl homologs show absorption bands in the region 1600-1550 cm^{-1}(due to C=N stretching). Pyrrolic absorption bands appear at 3460-3450 cm^{-1}(due to N-H stretching). Amides appear at 1730-1640 cm^{-1}(due to C=O) and at 3450-3405 cm^{-1} (due to N-H stretching in primary and secondary amides).

Moschopedis et al. (91) reported an infrared method for the identification of nitrogen functional groups in resin and asphaltene fractions of Athabasca bitumens. The fractions containing nitrogen compounds were separated from the bitumens and part of these fractions were trifluoroacetylated along with model nitrogen compounds. Both derivatized and underivatized samples and nitrogen compounds were subjected to infrared analysis. The comparative study of infrared spectra led to the identification of major compound types present in the samples. It was observed that the dominant nitrogen compound types present in the resins and asphaltenes of Athabasca bitumens are of carbazole type containing imino functional group.

Khan et al. (50,85) employed infrared spectroscopy for the qualitative determination of nitrogen compound types from acidic, basic and neutral fractions of both low- and high-boiling distillates of an Iraqi crude oil. As a result, several nitrogen compounds were characterized which include indoles, carbazoles, quinolines, benzoquinolines and five and six membered cyclic amides.

Amateis and Taylor (70) have used Fourier Transform Infrared Spectroscopy (FTIR) coupled with microbore liquid chromatography for the analysis of basic nitrogen compounds in coal-derived products. Separated compounds were characterized by comparing their spectra with those of model nitrogen compounds. The compounds identified were anilines, pyridines, quinolines and tetrahydroquinolines.

Strachan and Johns (83) used Infrared spectroscopy for the characterization of nitrogen compound types in coal-derived liquids. As a result of this study, several functionalities were identified.

Infrared spectroscopy has also been used for the quantitative estimation of nitrogen compound types. McKay et al. (40,41) have employed infrared method in combination with chromatography to analyze high-boiling petroleum distillates and residues both qualitatively and quantitatively for their acidic (40) and basic (41) nitrogen compound types. In these studies, crude oils from different origins were examined. Infrared spectra of acid and base subfractions were obtained in solutions. Quantitative Infrared spectra of model nitrogen compounds were recorded to obtain molar extinction coefficients of different functional groups present. This information along with average

molecular weight data obtained by mass spectrometry made it possible to analyze petroleum acids and bases quantitatively.

McKay et al. (92) have also reported quantitative infrared spectroscopy of acids separated from high-boiling distillates of shale oil. The method was similar to that used for petroleum acids (40). The compound types identified were pyrroles, phenols and amides.

Green et al. (71) reported the quantitative infrared spectroscopy of nitrogen compound types in solvent refined coal liquids and upgraded products. Quantitative infrared spectra of model nitrogen compound types were recorded at different concentrations and calibration curves were prepared for each compound type under determination. The overall method was quite similar to that of McKay et al. (40,41) except that dichloroethane was used as a solvent because dichloromethane, being more volatile, evaporate from the infrared cells and produced error the in results.

2.4.4 ULTRAVIOLET SPECTROSCOPY(UV)

Ultraviolet spectroscopy has also been used for the identification of nitrogen compound types. Many polycyclic nitrogen compounds absorb in the ultraviolet region and, therefore, can be subjected to ultraviolet spectroscopic analysis. These compounds have their maximum absorption at characteristics wavelength and therefore can be identified. Several investigators have reported the use of ultraviolet spectroscopy for the characterization of nitrogen compound types in crude oils and related materials.

Jewell and Hartung (93) used ultraviolet spectroscopy for the identification of nitrogen bases in heavy gas oil. Ultraviolet spectra of separated fractions were recorded along with those of pure nitrogen compounds expected in the fractions and were compared with each other. This led to the identification of various nitrogen compounds including quinolines, benzoquinolines, hydroquinolines, indoles and carbazoloquinolines.

Copelin (94) employed ultraviolet spectroscopy for the characterization of 2-quinolones in a California crude oil.

Snyder and Buell (29) employed ultraviolet spectroscopy to characterize compounds of nitrogen and oxygen in the distillates of California crude oil. The ultraviolet spectra of separated subfractions were compared with spectra of model nitrogen compounds. This comparison led to identification of many nitrogen compounds including alkyl homologs and benzologs of pyridine and pyrrole.

Schmitter et al. (54) used ultraviolet spectroscopy for the identification of major structural types of aza-arenes in fractions obtained from reverse phase liquid chromatography (RPLC) of petroleum bases. It was observed that structures with linear annelated aromatic rings such as acridines were easily distinguished from angular ring structures like phenanthridines. As a result of this study, aza-arenes having two to eight fused aromatic rings were characterized.

Khan et al. (50,85) have employed ultraviolet spectroscopy for the identification of nitrogen compound types in low and high-boiling petroleum distillates. In this study, several nitrogen compound types

were characterized from acidic, basic and neutral fractions of these distillates.

Gernot et al. (95) used ultraviolet spectroscopy to characterize nitrogen polycyclic compounds in Arab Light petroleum and this led to the identification of azaphenanthrene.

2.4.5 NONAQUEOUS POTENTIOMETRIC TITRATION(NAPT)

Potentiometric titration is indeed a remarkable analytical technique. Acidic and basic component of a sample can be titrated quantitatively and quickly. Titration of acids and bases in nonaqueous solvents compares favorably with aqueous titration in speed, accuracy and convenience. Moreover, solubility of organic compounds is rarely a problem with nonaqueous solvents and much weaker acids and bases can be titrated to a discernable equivalence point than is possible in aqueous solutions. This is because the potential ranges attainable in organic solvents are often much greater than in water. This makes it possible to titrate each compound in a mixture to a separate end point, provided there are significant differences in acidic or basic strength of the titratable compounds.

It is convenient to use the ionization constants that have been determined in aqueous solutions for various bases to predict the relative strength of these bases when titrated in a nonaqueous solvent. A large number of pKa values have been measured for bases in water but relatively few such data are available for nonaqueous solvents. Hall and Werner (96) and Streuli (97,98) have shown that a linear relationship exists when the HNP (half neutralization potential) values

in millivolts for a series of bases titrated in a nonaqueous solvent, are plotted against their pKa values in water. Half neutralization potential is the potential which corresponds to the mid point of the potentiometric titration curve. This holds good only for bases that are not levelled by a particular solvent. There are exception of course, but the linear relationship appears to be a good approximation for most compounds. This means that the titration behaviour of a base in a nonaqueous solvent may be predicted from its dissociation constant in aqueous solution. Perrin (99) has listed dissociation constants for approximately 3800 bases in water, so the scope of prediction is obviously broad.

Many investigators have employed nonaqueous potentiometric titration for the determination of nitrogen compounds found in petroleum and related materials. As a result, different classes of nitrogen compounds were determined both qualitatively and quantitatively. In all of these titrations, perchloric acid is used as the titrant either in acetic acid or in dioxane (1,4-dioxane). Acetic acid has levelling effect on mixture of certain bases and in such cases, perchloric acid in dioxane is a good titrant. In order to permit titration of a weak base, the solvent should have as weakly basic properties as possible. Different solvents have been used either as pure or in mixture such as acetonitrile (100,101), nitromethane (97), acetophenone and nitrobenzene (102), acetone (103), chlorobenzene (104) and acetic anhydride (41,69,98,105,106) for the titration of nitrogen bases.

Kolthoff et al. (100) used acetonitrile for the titration of mixtures of aliphatic and aromatic nitrogen bases. The titrant used was perchloric acid in acetic acid containing two percent acetic anhydride.

Fritz (101) employed acetonitrile as a solvent for the titration of aliphatic and aromatic amines and was found to fulfill all the requirements of a good differentiating solvent for amines. Mixtures containing strong and weak nitrogen bases were differentiated very well in this solvent.

Wimer (105) used pure acetic anhydride as a solvent for the titration of aliphatic amines and amides. The titrations were rapid and reproducible. The results suggested the possibility of determining amides and amines in complex mixtures. Acetylation of amines was prevented by titrating at zero centigrade.

Streuli (98) titrated a number of neutral and anionic bases in acetic anhydride. Anions appeared stronger bases in this solvent than in water as compared to neutral compounds.

Streuli (97) employed nitromethane as a solvent for the titration of amines, amides and other organic nitrogen bases. The titrant used was perchloric acid in nitromethane. It was observed that nitromethane is an excellent solvent for the titration of weak organic bases like amines, amides and ureas. These nitrogen compounds showed relatively greater basicity in this solvent than they do in water. Amines exhibited normal behaviour in this solvent but substituted amides showed steep titration curves which may be due to the hydrogen bonding between solute molecules.

Fritz and Streuli (103) used pure acetone as a solvent for the titration of bases and especially for the differentiation of mixtures of aliphatic and aromatic amines. The titrations were carried out by

perchloric acid both in dioxane and glacial acetic acid separately. These titrations were followed visually or potentiometrically. Titration in this solvent resulted in better differentiation of mixtures of aliphatic and aromatic amines compared to other solvents.

Buell (106) employed differential nonaqueous potentiometric titration for the analysis of nitrogen compounds in petroleum. This was accomplished by titrating different fractions with perchloric acid in dioxane using acetic anhydride-benzene and acetonitrile-benzene solvent systems separately. Perchloric acid in acetic anhydride permitted the titration of all basic nitrogen containing compounds but acetylated some primary and secondary amines. This reaction converted some of the more basic compounds to amides which are very weak bases but these compounds still can be titrated quantitatively. Perchloric acid in acetonitrile did not cause acetylation and did not titrate very weak bases. Therefore, the very weak bases in a fraction were obtained by subtracting the amount of total base determined in acetic anhydride from that found in acetonitrile. Nonbasic nitrogen was found by subtracting the amount of basic nitrogen titrated in acetic anhydride from the total nitrogen in the fraction. This scheme categorized all titrated compounds into five classes based on their pKa values and titration in different solvents.

McKay et al. (41) have used a mixture of acetic anhydride and benzene in the volume ratio two to one(2:1) as a solvent for the titration of nitrogen bases in high-boiling petroleum distillates from different crude oils. Bases having HNP values of 370 mv or less were regarded as strong while those having HNP above 370 mv were

classified as weak bases. The results were compared with those obtained from quantitative infrared analysis and were found in good agreement.

Darlage et al. (102) have used acetophenone and nitrobenzene as the solvents for the nonaqueous potentiometric titration of coal-derived asphaltenes and various model nitrogen compounds. The titrant was perchloric acid in dioxane. Several nitrogen-containing compounds with a wide range of basicities were titrated in acetophenone and nitrobenzene separately. Based on their pKa and half neutralization potential values, these compounds were divided into five classes.

Holmes and Thompson (69) have employed the method of Buell(106) for the determination of basic and nonbasic nitrogen compound in shale oils and by Heppner (107) for the analysis of nitrogen containing compounds in shale oil.

Dutta and Holland (104) have studied acid-base characteristics of petroleum asphaltenes using differential nonaqueous potentiometric titration. Pure chlorobenzene and mixture of chlorobenzene and acetic anhydride in the volume ratio nine to one (9:1) were used as titration solvents for basic functionalities separately. The titrant used was perchloric acid in dioxane and the primary standard was N-phenylguanidine. As a result, the bases titrated were categorized into strong, weak and very weak on the basis of their pKa values. The strong bases include pyridines, imidazoles, aliphatic and aromatic amines. The weak bases titrated were caffeine and phenazines while the very weak bases found were acetanilides and N-methylacetanilides.

Green et al. (71) have also used the method of Buell(106) for the titration of nitrogen compounds in coal liquids. The overall method was similar except that different electrodes were used.

It has been demonstrated by several investigators that presence of acetic anhydride in the titration mixture increases the potential range of the solvent in both acidic and basic directions (108). Thus going through the literature, it was found that acetic anhydride is a good solvent for the titration of strong as well as weak bases and it is the one commonly used by the investigators. Acetic anhydride has a dielectric constant of 20.7 (109) which permits reproducible measurements of potential with a calomel-glass electrode system. The relatively large specific conductance of acetic anhydride, 4.8×10^{-7} mho indicates slight autoprotolysis to yield acetyl (CH_3CO^+) and acetate (CH_3COO^-) ions (110). Acetic anhydride has been used previously as a titration medium, either alone or in conjunction with other solvents. A number of compounds which do not exhibit basic properties in water, acetic acid and acetonitrile, may be quantitatively titrated in this solvent. The draw back of this solvent is its reactivity with some compounds to produce new products, usually weaker bases, but the products of acetylation are still reasonably strong bases and are titrated quantitatively (98). Titration for samples which do not undergo acetylation, may be considered quantitatively. The lower dielectric constant of acetic anhydride favors the formation or retention of uncharged species and therefore increases the base strength of anions in general. The absence of water from this solvent system also permits the titration of bases weaker than water (98). It has been observed

that pure acetic anhydride is advantageous for titration of amides, tertiary amines and certain other weak bases (105). This is because high anhydride concentration favors the formation of acetyl (CH_3CO^+) as acetyl perchlorate and thus maximum changes in end point potentials are observed. This led to better differentiation of strong and weak basic compounds present in the sample.

Similarly 1,4-dioxane is the solvent commonly used for the preparation of perchloric acid solution. Dioxane has a dielectric constant of 2.2 and is not amphiprotic. It is very weakly basic and reacts with perchloric acid to form solvated proton and the acid anion. Because of very low dielectric constant, this ion pair is probably not dissociated to any significant extent. The reaction of a base in dioxane solution of perchloric acid may be viewed as simply the replacement of the weaker base, dioxane in the ion pair by the stronger base present in the sample.

2.4.6 GAS CHROMATOGRAPHY(GC)

Gas chromatography with a selective nitrogen detector is a sensitive, rapid and accurate analytical approach to the analysis of nitrogen compounds in petroleum. The introduction of thermionic detector (Nitrogen phosphorus detector (NPD)) by Kolb and Bischoff (111) which uses a rubidium silicate bead as the alkali source, has greatly increased the capability of detecting nitrogen compounds in complex mixtures which may be composed predominantly of hydrocarbons. The usage of NPD for the detection of nitrogen compounds in a matrix of hydrocarbons require maximizing the nitrogen

response and minimizing the hydrocarbon response. It is possible to reduce the hydrocarbon response to zero and to have detectable response of nitrogen compounds.

Baker (112) has reported that response is not necessarily correlated with the number of nitrogen atoms in a molecule. Response also varies with type of nitrogen-containing compounds. It was observed that those nitrogen compounds whose structures are favourable for the formation of cyano radicals, offer greater response than those unfavour cyano radicals formation. So that if one is investigating a specific compound or a class of compounds, it would be better to optimize the system with that compound or a member of that class of compounds. Many investigators have employed NPD for the analysis of complex mixtures.

Albert (113) used NPD along with flame ionization detector for the determination of nitrogen compounds in light catalytic cycle oil and light vacuum gas oil. The dominant nitrogen compound types (pyridines, quinolines, indoles and carbazoles) were characterized by boiling points and carbon numbers. Synthetic mixtures of nitrogen compounds were also chromatographed to determine the relative response of each type of compounds. Effect of alkyl substituents on the detector response was also determined. This study offers a fast and reproducible method for the characterization of nitrogen compounds in petroleum and related materials.

2.4.7 GAS CHROMATOGRAPHY-MASS SPECTROMETRY(GC-MS)

The group type analysis of nitrogen polycyclic compounds in complex mixtures has provided a great amount of information concerning

their general composition. However, the exact identification and quantification of individual constituents is most desirable. The only method that can even approach this task today is combined gas chromatography-mass spectrometry. The use of high-resolution capillary gas chromatographic columns has greatly increased during the last several years. The maximum resolution of mixture components before mass spectral analysis is of utmost importance in providing unambiguous identification of individual compounds. The mass spectrometer is unable to provide the correct composition of a mixture by itself and, therefore, prior separation by high resolution capillary columns is essential. The power of the gas chromatography-mass spectrometry system for the analysis of complex mixtures is demonstrated by various applications found in the literature.

Bertsch et al. (114) analyzed coal-derived fluids by high resolution gas chromatography-mass spectrometry using glass capillary columns before and after liquid chromatography on silica gel. The bulk of the sample was characterized as compounds of nitrogen and oxygen along with few hydrocarbon compound types.

Schiller (65) employed gas chromatography-mass spectrometry for the analysis of coal-derived liquids. Mass spectra were recorded for large peaks which appeared in each chromatogram. A number of nitrogen compounds were separated and identified including quinolines, benzoquinolines, carbazoles and benzcarbazoles.

Gas chromatography-mass spectrometry has also been used for the identification of nitrogen polycyclic compounds in air borne particulate

matter (115), tobacco and smoke condensate (116,117) and PVC smoke particulates (118) in which a number of these compounds have been characterized.

Borwitzky and Schomburg (119) have developed a method for the qualitative analysis of coal tar using glass capillary chromatography combined with mass spectrometry. The method employed thermally stable wall coated open-tubular(WCOT) columns. More than 140 components including several heterocyclics were separated and characterized. Comparison of the retention times of model compounds led to the characterization of major peaks in mass chromatogram. The nitrogen compounds characterized included azafluorene, acridine, quinoline, benzoquinoline and dibenzoquinolines.

Ho et al. (23) reported gas chromatographic-mass spectrometric characterization of neutral nitrogen compounds separated from synthetic crude oils. Several nitrogen compounds were identified belonging to different classes. The results indicated that shale oil contains mostly alkyl substituted indoles, carbazoles and benzcarbazoles while coal-derived liquid contains alkylindoles, phenyl substituted pyrroles and indoles, alkylcarbazoles and alkylbenzcarbazoles.

Shue and Yen (120) have used GC-MS technique for the identification of nitrogen-containing compounds in shale oil. The method aided in the identification of pyridine homologs and benzologs as the major components present.

Schmitter et al. (121) used gas chromatography-mass spectrometry for the analysis of nitrogen bases from petroleum. The bases were

separated by reverse phase liquid chromatography of crude oils. A number of aza-arenes were separated and characterized in this study.

Yen et al. (122) used GC-MS for the identification of nitrogen containing compounds from shale oil. It was found that pyridine was the basic nucleus of most of the nitrogen compounds present in different fractions. The compounds characterized were mostly alkyl homologs and benzologs of pyridines.

Grimmer et al. (95) reported capillary gas chromatographic-mass spectrometric characterization of aza-arenes in Arabian Light petroleum. After the enrichment of aza-arenes, the material was subjected to GC-MS analysis and mass spectra were obtained for separated components. From the fragmentation pattern, it was infered that the nitrogen compounds present in these fractions belong to five CH_2-homolog series. These series were 4-azaphenanthrene, azapyrene/azafluoranthene, azadibenzothiophene. azachrysene/azabenz[a]anthracene/azatriphenylene and azabenzopyrene/azabenzofluoranthene.

Burchill et al. (51,52) reported a detailed study of nitrogen compounds present in coal tar products. Investigation of nitrogen compounds was carried out both in unfractionated materials (51) and separated basic fractions (52). Identification of individual nitrogen compounds was achieved using gas chromatography-mass spectrometry. In order to distinguish between the possible nitrogen compound types for a given atomic composition, boiling points of the compounds were considered. The method led to identification of several nitrogen heterocyclics of both pyridine and pyrrole types.

Das et al. (53) characterized coal tar nitrogen bases using gas chromatography-mass spectrometry technique. The scheme involved acid extraction of bases, their fractionation and derivatization. The compounds identified were from ten nitrogen compound types belonging to eighteen homolog series which included alkylamino derivatives of pyridine, benzoquinoline, azafluorene, naphthalene and anthracene.

2.4.8 MASS SPECTROMETRY(MS)

In recent years, a number of mass spectrometric methods have been successfully applied to the analysis of complex mixtures like petroleum and shale oils. The mass spectrometric analysis is based on the fact that the organic molecules are transformed into organic ions in the mass spectrometer using different techniques which include electron ionization, chemical ionization, field ionization and field desorption. These ions, consequently, are sorted out by the instrument according to their mass to charge (m/e) ratios. These ions are characteristics of the compounds or compound types in most of the cases. So by comparison, individual compounds or compound types can be characterized. In literature, both low resolution and high resolution mass spectrometry has been used for the identification of nitrogen-containing compounds.

Nagy and Gagnon (123) have reported low resolution electron impact mass spectrometric analysis of Athabasca petroleum deposits. The compounds were characterized by the characteristic fragments present in the mass spectra of the samples. Quantitative analysis of the samples was made by a matrix computation method based on the characteristic

peaks of the pure compounds.

Peters and Bendoraitis (61) employed high resolution mass spectrographic method for analysis of nitrogen-containing compounds. The method was applied to petroleum samples and shale oils and a number of nitrogen compounds were characterized.

Goncharov et al. (124) employed low resolution electron impact mass spectrometry for the analysis of nitrogen bases isolated from crude oils of various deposits in soviet union. The compounds identified belong to quinoline and acridine series. It was observed that the amount and types of nitrogen bases differ in oils of various deposits.

Yoshida et al. (125) have employed field ionization and field desorption mass spectrometry for the analysis of fractions obtained from liquid chromatography of coal-derived liquids. These techniques provided the exact molecular weight distribution profiles of chromatographic fractions and the average molecular weights calculated were close to those obtained from vapor pressure osmometry. These methods produced reliable mass spectra which resulted in the group type analysis of these fractions.

Beiko et al. (56) have employed low resolution electron impact mass spectrometry for the characterization of nitrogen basic compounds separated from low boiling distillate of Uzbekistan crude oil. The compounds identified were mostly alkyl homologs of quinoline and thiazole.

Grisby et al. (126) have used fast atom bombardment mass

spectrometry (FABMS) for the characterization of nitrogen compounds in fossil fuels. The compounds were characterized by comparing FABMS spectra of model nitrogen compounds with those obtained from the sample. characterization was made on the basis of $M^{+\cdot}$, $(M+H)^{+\cdot}$ and $(M-H)^{+\cdot}$ ion peaks. This study resulted in the identification of several classes of nitrogen-containing compounds.

Bianco et al. (59) have employed low resolution mass spectrometry for the characterization of basic nitrogen compounds in coal-derived liquids. The sample was both in derivatized and underivatized forms. Several nitrogen compounds were identified including azapyrenes, acridines, quinolines and anilines.

CHAPTER 3

OBJECTIVES OF THE STUDY

The elucidation of the chemical structure of nitrogen compounds is of great importance. It is also a challenge to the analysts because these compounds are present in low quantity in most of the crude oils and occur as complex mixtures.

The objective of this research is to selectively separate the nitrogen compounds obtained from high-boiling distillates of Saudi Arabian crude oils into different types such as acidic, basic and neutral fractions. Each fraction will be further separated into meaningful compound types using high performance liquid chromatography. The subfractions thus obtained will be classified into different compound types such as pyridine, pyrrole and amide. The chromatographic-infrared method will be used for the analysis of HPLC fractions. Identification of compound types and/or individual compounds in each fraction will be made. The research plan consists of the following steps.

1. Literature Survey
2. Development of analytical procedures using authentic model compounds.
3. Characterization of Saudi Arabian crude oils and preparation of high-boiling distillate cut (370-535°C) for each crude being studied.
4. Selective separation of distillate cuts into basic and nonbasic nitrogen compounds using ion-exchange and complexation chromatography.

5. Further fractionation of nitrogen compounds into nitrogen compound types using HPLC.
6. Identification of compound types or individual compounds in each fraction using IR, GC and GC-MS methods of analysis.

The crude oils considered in this work are Saudi Arabian crude oils from ARAMCO export quality. The boiling range of interest is the material boiling between 370°C (700°F) and 535°C (1000°F). The methods used for the analysis will include nonaqueous potentiometric titration, vapor pressure osmometry, infrared and ultraviolet spectroscopy, gas chromatography, mass spectrometry and gas chromatography-mass spectrometry.

Preliminary work will be done on the following four crude oils.

1. Arab Heavy (AH)
2. Arab Medium (AM)
3. Arab Light (AL)
4. Arab Berri (AB)

The preliminary work will include the following determinations:

1. Characterization of crude oils for general properties
2. Distillation and preparation of distillate cuts
3. Elemental analysis
4. Nonaqueous potentiometric titration
5. Molecular weight determination

Detail characterization studies of the nitrogen compound types will be done for Arab Heavy and Arab Medium crude distillates only. These cuts will be selectively separated into further fractions using different separation schemes and individual fractions will be analyzed for

individual compounds and/or compound types by various techniques such as

1. Infrared Spectroscopy
2. Ultraviolet Spectroscopy
3. Nonaqueous Potentiometric Titration
4. Gas Chromatography
5. Gas Chromatography-Mass Spectrometry

CHAPTER 4

EXPERIMENTAL

4.1 DISTILLATION OF CRUDE OILS

4.1.1 TRUE BOILING POINT DISTILLATION(TBP)

APPARATUS

The apparatus used for true boiling point distillation of the crude oils was an all-glass semi-cal 3650 serial 298 (Podbielniak Inc. Illinois, USA) and the method used was ASTM D2892-78 (127). This apparatus consists of a packed column having a fractionation efficiency of 15 theoretical plates, a three-neck distillation kettle of 5.0 litre capacity and heating mantles. The column was 3.3 ft x 1.0 inch and packed with Heli-Pak 2917, 0.05 x 0.10 x 0.10 inch made from Nichrome. The column is connected to two distillate receivers, each of 200 ml capacity to obtain the desired distillation cuts from the column. This apparatus is shown in Figure 1.

PROCEDURE

The overall distillation conditions are given in Table 1. A 4.0 litre sample of Arab Heavy crude oil was taken from the container after shaking it properly and weighed. This sample was transfered to the distillation kettle. The distillation kettle was connected to the column. The kettle was also provided with a thermometer and nitrogen supply. The kettle was covered by heating mantles from top and bottom to heat the whole crude oil uniformly. The distillate receivers were also

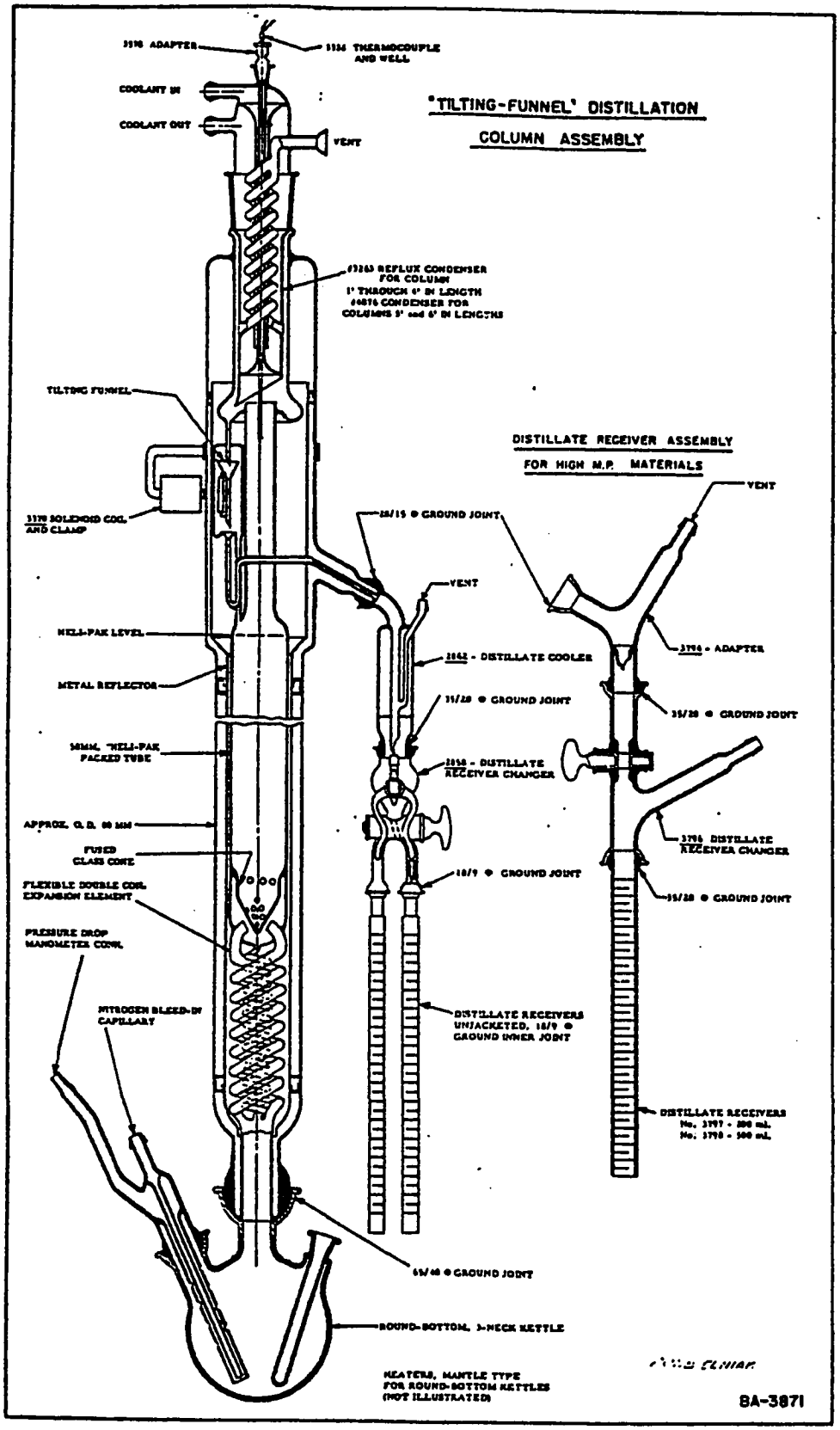


Figure 1. True Boiling Point (TBP) Distillation Apparatus

TABLE 1

CRUDE OIL DISTILLATION CONDITIONS

Apparatus Used	: All-Glass Semi-Cal 3650 Serial 298 (Podbielniak)
Method Employed	: ASTM D2892-78
Distillation Kettle	: 5.0 Litres
Efficiency	: 15 Theoretical Plates
Reflux Ratio	: 5:1

ATMOSPHERIC DISTILLATION

Vapor Temperature	: 200°C (maximum)
Kettle Temperature	: 280°C (maximum)

VACUUM DISTILLATION ON TBP APPARATUS

Pressure	: 30-40 mm Hg
Vapor Temperature	: 200°C (maximum)
Kettle Temperature	: 280°C (maximum)

VACUUM DISTILLATION ON WIPED-FILM MOLECULAR STILL

Pressure	: 0.1 mm Hg

1st Distillation at 140°C(285°F) to get

370°C+(700°F+) Residue

2nd Distillation of Residue at 260°C(500°F) to get

370-535°C(700-1000°F) Distillate Cut

connected with the column. All the connections were checked and heating of the oil was started. The distillation was carried out initially at atmospheric pressure. The distillation was continued at the maximum kettle temperature of 280°C and the 200°C vapor temperature. Above this temperature, the cracking of the crude components was expected, so the distillation was stopped and the kettle was allowed to cool. Distillation was restarted at reduced pressure using a vacuum pump. A pressure of 30-40 mm Hg was maintained throughout the vacuum distillation at TBP apparatus. The reduced pressure was necessary to distil the crude oil at higher temperature while reducing the possibility of thermal cracking of the material. A reflux ratio of 5:1 was maintained throughout the distillation on TBP apparatus both at atmospheric and under vacuum. During the distillation process, pure nitrogen gas was allowed to bubble slowly through the crude oil in the kettle to facilitate the boiling and to remove trace oxygen present in the oil. The distillation was continued until the vapor temperature of 200°C and kettle temperature of 280°C was reached.

4.1.2 WIPED-FILM MOLECULAR STILL DISTILLATION

The TBP apparatus cannot be used to obtain high-boiling fractions because at high temperature, severe cracking takes place due to the prolonged heating of the material present in the kettle. To avoid overheating, one has to turn to conditions where the sample remains on the heating surface for a short period of time. The distillation should be carried out under vacuum, high enough to allow the volatiles to leave the hot surface and condense on a cold surface. This technique of distillation is called wiped-film and it is widely used for the distillation

of high-boiling materials.

APPARATUS

The distillation apparatus is shown in Figure 2. This apparatus is called Wiped-Film Molecular Still. It consists of a feed and degaser flask at the top of the apparatus and it is connected to the main body of the still(evaporator) through a narrow tube provided with a valve which allows the feed to the evaporator. The evaporator contains three sets of teflon wipers placed on the vertical axes and connected to a drive unit which rotates these wipers at constant speed. At the bottom, the evaporator is provided with two receivers, one for distillate and the other for residue. The apparatus is provided with a high efficiency vacuum pump which consists of a rotary pump and a diffusion pump.

PROCEDURE

The whole apparatus was checked for its connections and all joints were vacuum sealed. The valve between the feed flask and the evaporator was closed. The residue obtained from the TBP distillation was charged to the feed and degaser flask. The main body of the still, the evaporator, and the feed flask were covered with heating mantles from all sides to achieve uniform and constant heating of the feed. The heating mantle of the evaporator was provided with a thermocouple to recorded the temperature. All joints of the whole assembly were again checked for any possible leak. The vacuum pump was started to provide high vacuum to the system and the heating of the feed and the evaporator was also started. When the whole apparatus maintained a constant high vacuum of 0.1 mm Hg and the evaporator achieved the

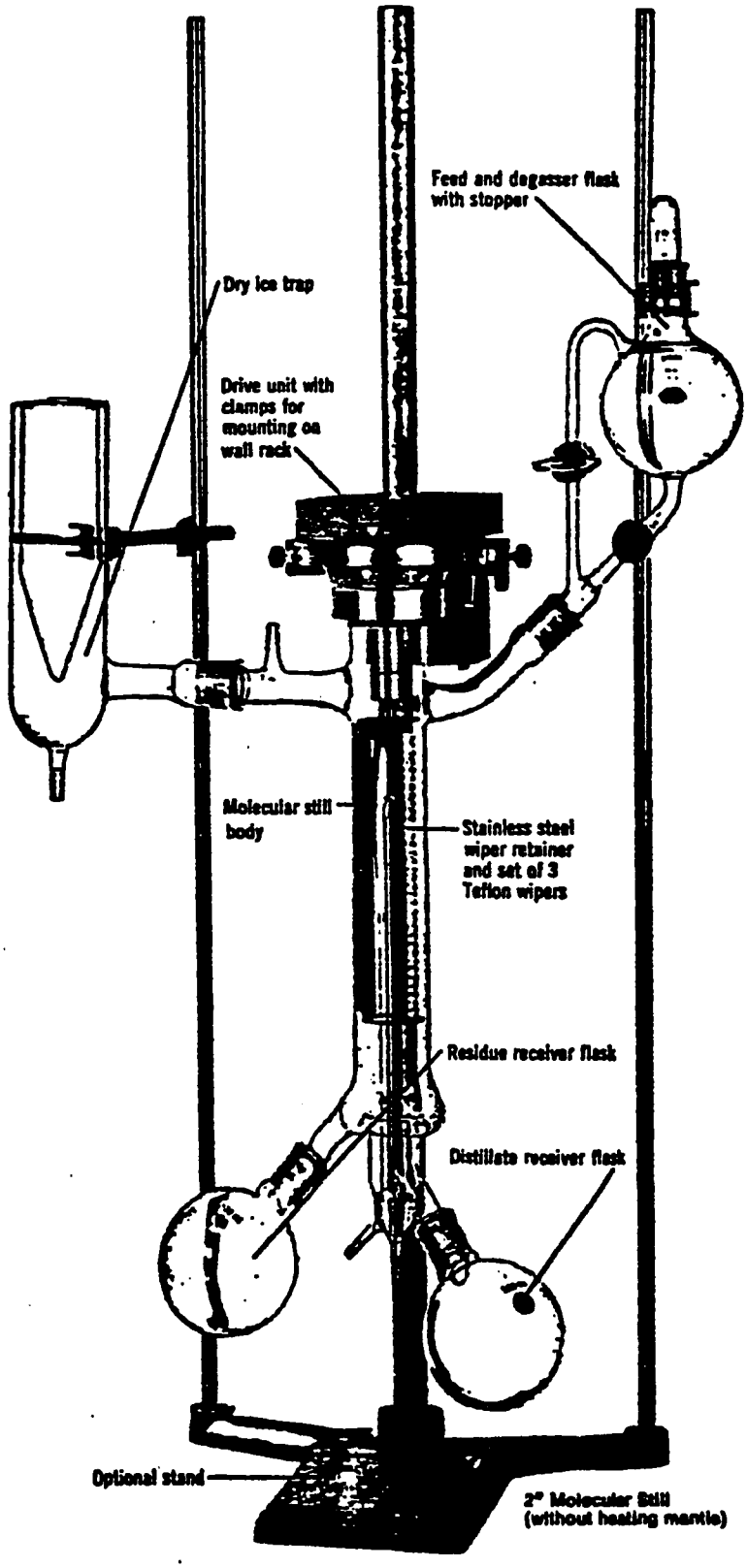


Figure 2. The Pope Wiped-Film Molecular Still

desired temperature of 140°C, then the drive unit was started to rotate the wipers. The temperature of 140°C at 0.1 mm Hg equals 370°C at atmospheric pressure. This temperature of the evaporator was maintained to remove the material boiling below 370°C. The feed from the flask was introduced into the evaporator slowly at a constant rate keeping the temperature and the pressure accordingly. The wipers spread the feed as a thin film on the heated walls of the evaporators. The volatile portion of the feed was vaporized and condensed on an inner cold surface which was concentric to the heated evaporator. The surface was cooled by recirculating water from the tap. The condensed material which was the distillate(boiling point < 370°C), flowed along the cold surface downwards and collected in the receiver at the bottom. The material left on the heated walls which was the residue(370°C+), flown through the walls and collected in the second receiver at the bottom. The distillation was continued in this way until the end of the feed in the flask. The process was repeated to remove any material present below 370°C in the residue. The 370°C+ residue was distilled through the wiped-film molecular still at 0.1 mm Hg pressure and 260°C temperature to obtain the distillate cut in the boiling range 370-535°C. The whole process on the molecular still was repeated several times to collect sufficient amount of distillate needed for the analysis. The distillation was carried out for all four crude oils using the same procedure and same conditions to collect the distillate cuts in the boiling range 370-535°C.

4.1.3 BOILING RANGE DISTRIBUTION OF DISTILLATES (370-535^{O}C) (SIMULATED DISTILLATION)

The Arab Heavy and Arab Medium distillates were subjected to simulated distillation by gas liquid chromatography. The purpose was to confirm the boiling range of the materials. The system used was HP-5880 gas chromatograph. The operating conditions employed for simulated distillation are given in Table 2. The method employed was ASTM D2887-73 (128). Briefly speaking, the sample (distillate dissolved in toluene) of 0.3 microlitre was introduced into the gas chromatograph. The initial temperature of the column was 35^{o}C and it was programmed at a rate of 10^{o}C/min up to the maximum of 350^{o}C. The final temperature was maintained for 10 minutes. The gas chromatograph separated the hydrocarbons present in the sample in boiling point order. Boiling temperatures were assigned to the time axis from a calibration curve obtained under the same conditions by running a known mixture of hydrocarbons covering the boiling range expected in the sample. This led to formation of boiling range distribution curve for the distillate. The area under the curve was recorded continuously throughout the run. The point at which the cumulative area count was 0.5 percent of the total area, was assigned as initial boiling point whereas the point corresponds to cumulative area count of 99.5 percent of the total area was recorded as final boiling point of the sample.

4.2 ISOLATION OF NITROGEN COMPOUNDS FROM HIGH-BOILING DISTILLATES(370-535^{O}C)

The distillate cuts were separated into fractions that are definable

TABLE 2

SIMULATED DISTILLATION CONDITIONS

Instrument	: HP-5880 Gas Chromatograph
Method Employed	: ASTM D2887-73
Detector	: Flame Ionization Detector(FID)
Column	: Stainless Steel Tubing 20 inch long , 0.12 inch i.d.
Packing Material	: 10% UC-W980 Silicon Rubber 80-100 mesh Chromosorb P-AW
Flow Rates(cm^3/min)	
Air	: 400
Hydrogen	: 30
Helium(Carrier)	: 25
Temperatures(^oC)	
Injector	: 350
Detector	: 350
Column	
Initial Temperature	: 35
Programming Rate	: 10^oC/min
Final Temperature	: 350
Final Time	: 10 min
Injection Volume	: 0.3 microlitre

according to the type of compounds they contain. The distillate cuts were subjected to successive separation steps using chromatographic methods to remove and recover most of the nitrogen compounds as acids, bases and neutral nitrogen compounds. The acids and bases were removed with anion and cation-exchange resins respectively while the neutral nitrogen compounds were obtained by coordination complex formation with ferric chloride supported on Attapulgus clay. The ion-exchange resins, both anionic and cationic, and the ferric chloride-Attapulgus clay complex were prepared prior to pack in the column. The various fractions obtained were freed of solvent using rotary evaporator at reduced pressure followed by nitrogen gas sweep at room temperature. The dried fractions were weighed to provide data on the composition of the distillate cuts.

APPARATUS AND MATERIALS

The anion-exchange resin was Amberlyst A-27 and the cation-exchange resin was Amberlyst A-15 and were obtained from Rohm and Haas, Inc. The ferric chloride hexahydrate was reagent grade obtained from Fisher Scientific. The Attapulgus clay was obtained from Englehard Minerals and Chemicals. Reagent grade n-pentane, supplied by Fisher Scientific, was further purified by flash distillation and by percolating through activated silica gel. Benzene (Merck) and Methanol (Fluka A.G.) were reagent grade and were flash distilled. The chromatographic column used for the separation was of 1.4 cm i.d. and 119 cm long made of glass. The column was water-jacketed and contained a recycling arrangement that allowed continuous elution of the sample without the need for large quantities of eluting solvent. The

chromatographic column is shown in Figure 3. All separations were carried out under an atmosphere of nitrogen free from oxygen and the chromatographic column was initially purged with nitrogen.

4.2.1 PREPARATION OF RESINS

4.2.1.1 ANION-EXCHANGE RESIN

The Amberlyst A-27, a strong anion-exchange resin, was thoroughly washed four times with a methanolic hydrochloric acid solution (10 volume percent hydrochloric acid in methanol) to ensure that all the active sites have only chloride ions. The resin was then washed and rinsed with distilled water (40 washings) until the washings were neutral to pH paper (83). The resin was activated with methanolic hydroxide solution (10 weight percent potassium hydroxide in methanol) to replace all chloride ions by hydroxyl ions. The resin was again washed with distilled water until the washings were neutral to pH paper. Finally, the activated resin was conditioned by sequential soxhlet extraction for 24 hours with each of the following solvents namely methanol, benzene and n-pentane. The resin was kept moist in n-pentane in order to avoid the production of artifacts that may result from resin decomposition (129).

4.2.1.2 CATION-EXCHANGE RESIN

The Amberlyst A-15, a strong cation-exchange resin, was thoroughly washed four times with a methanolic hydroxide solution (10 weight percent potassium hydroxide in methanol) to ensure that all the active sites have only potassium ions. The resin was then washed and

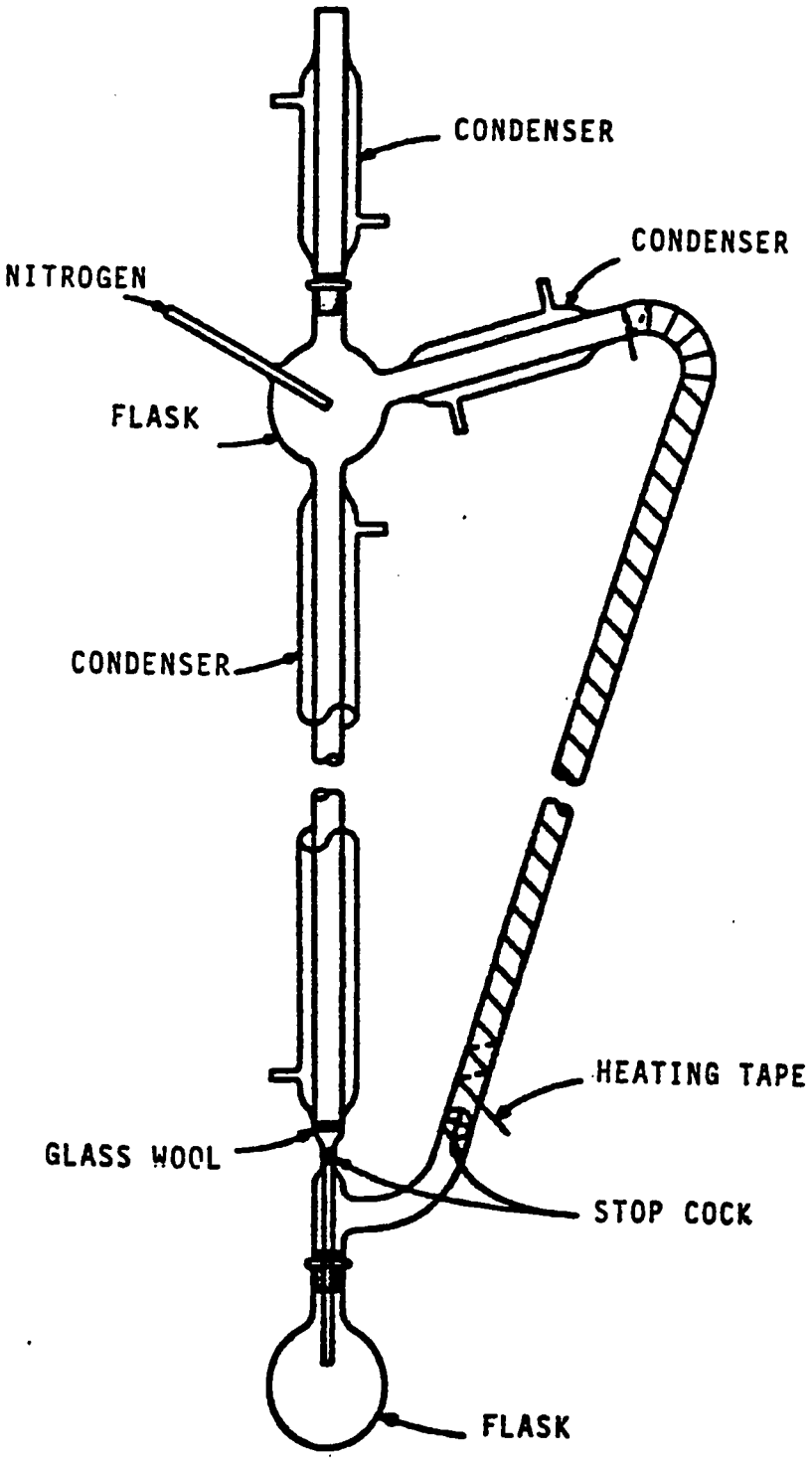


Figure 3. The Glass Chromatographic Column with Recycling Arrangement

rinsed with distilled water until the washings were neutral to pH paper. The resin was then soxhlet extracted with methanol for 24 hours. The resin was activated by adding it slowly to a solution of 10 volume percent hydrochloric acid in methanol. Slow addition was a precautionary step because this reaction was exothermic. The activation replaced all potassium ions for hydrogen ions. The resin was then washed with distilled water until the washings were neutral to pH paper. Finally, the activated resin was conditioned by sequential soxhlet extraction for 24 hours with each of the following solvents: methanol, benzene and n-pentane. The resin was kept moist in n-pentane in order to avoid the production of artifacts that may result from resin decomposition (129).

4.2.1.3 FERRIC CHLORIDE-ATTAPULGUS CLAY COMPLEX

Attapulgus clay (50-80 mesh) was contacted for one hour with a methanolic ferric chloride solution(10 weight percent ferric chloride hexahydrate in methanol). This led to the formation of a complex between ferric chloride and Attapulgus clay. The ferric chloride-Attapulgus clay complex was filtered and washed several times with methanol. Finally, the complex was soxhlet extracted with n-pentane for 48 hours to remove uncomplexed metallic salt. The complex material was dried at room temperature and was kept in nitrogen atmosphere.

4.2.2 SEPARATION PROCEDURES

The overall separation scheme is given in Figure 4. This scheme separated acids, bases and neutral nitrogen compounds from the distillates in subsequent steps.

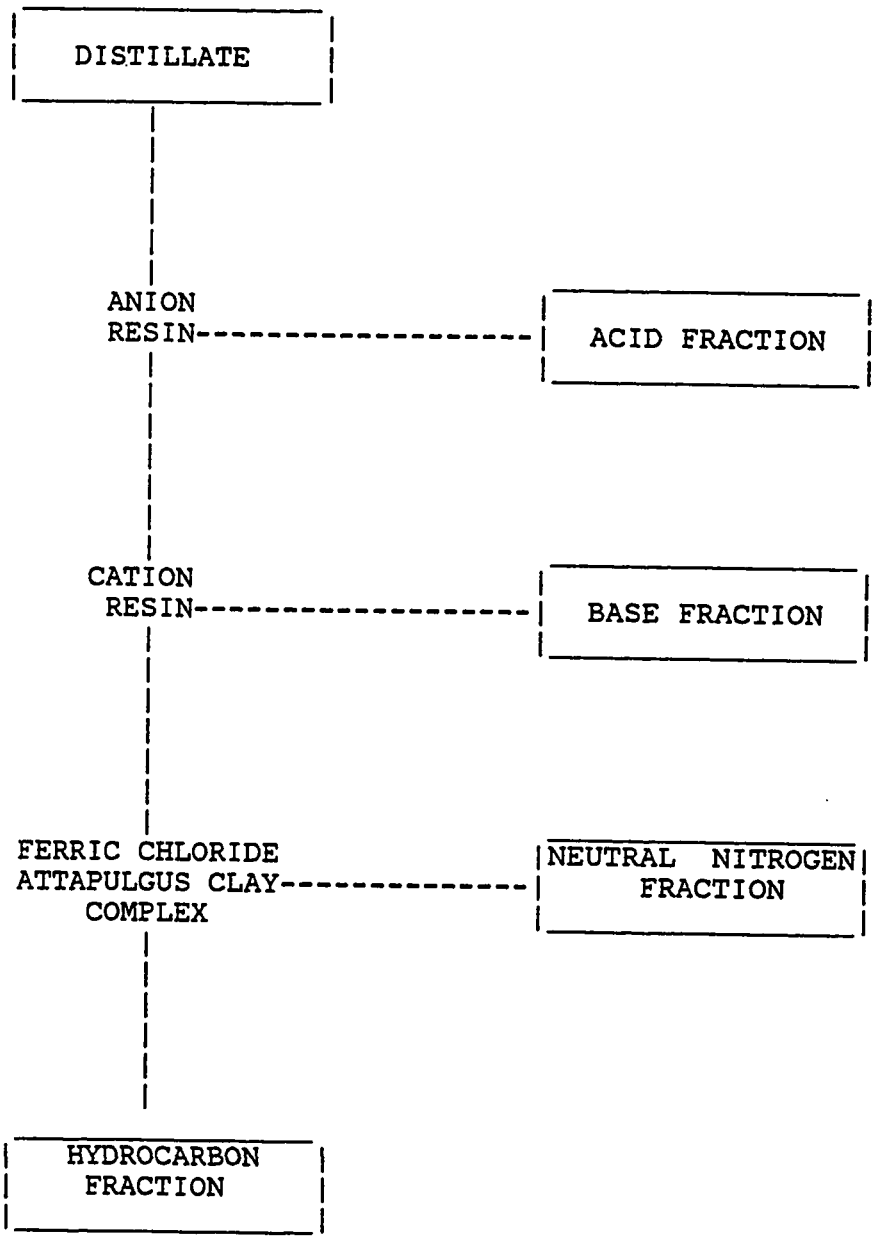


Figure 4. Scheme for the Separation of High-Boiling Distillates (370-535°C) into Acids, Bases and Neutral Nitrogen Compounds.

4.2.2.1 SEPARATION OF ACIDS BY ANION EXCHANGE CHROMATOGRAPHY

The chromatographic column was washed thoroughly with n-pentane and plugged with glass wool. The column was then purged with nitrogen gas. The column was packed with 80 grams of activated anion-exchange resin, A-27 moist in n-pentane under an atmosphere of nitrogen. The spacing and the air bubbles inside the column were removed using electric vibrator. The column was stabilized by n-pentane elution for 20 minutes. A sample of distillate (20 grams) was dissolved in 250 mls of n-pentane and stirred on magnetic stirrer. The solution was charged to the column in 100 mls portions and was eluted through the column at a rate of 2 ml/minute. Unreactive material was washed from the column with 400 mls of n-pentane for 40 hours using the recycling arrangement of the column at the similar rate used for elution. After removal of unreactive material (acid free distillate), the reactive compounds (acids) were recovered by elution with a mixture of ethylene chloride, methanol and toluene in the volume ratio of 2:1:1 for 70 hours (86). During the elution, care was taken to prevent the column from drying. The acids were obtained by removing the solvent on rotary evaporator at 40^{o}C at reduced pressure.

4.2.2.2 SEPARATION OF BASES BY CATION EXCHANGE CHROMATOGRAPHY

The procedure for the removal of bases from the distillate was similar to that used for acids. The sample of acid-free distillate was charged to the column already wet packed with activated cation-

exchange resin, A-15 and was eluted through the column at a rate of 2 ml/minute. Unreactive material (acid base-free distillate) was washed from the column with 400 mls of n-pentane for 40 hours using the recycling arrangement. After removal of unreactive material, the reactive compounds (bases) were recovered by elution with a mixture of 1,2-dichloroethane, methanol, toluene and isopropylamine in the volume ratio of 8:5:5:2 for 70 hours (86). Before removal of reactive material, nitrogen gas was forced up through the column to loosen the resin bed. This was a precautionary procedure to prevent the breakage of the column due to the swelling of resin in methanol and because of the exothermic reaction of the resin with isopropylamine. During the elution, care was taken to prevent the column from drying. The bases were obtained by removing the solvent on rotary evaporator at 40°C at reduced pressure.

4.2.2.3 SEPARATION OF NEUTRAL NITROGEN COMPOUNDS BY FERRIC CHLORIDE COORDINATION CHROMATOGRAPHY

The chromatographic column was the same as described previously. 50 grams of the anion-exchange resin, A-27 moist in n-pentane was packed into the chromatographic column under an atmosphere of nitrogen. The column was stabilized by n-pentane elution. Then 70 grams of ferric chloride-attapulgus clay complex was packed on top of the resin. A layer of glass wool was used to separate the two material. The sample of acid and base-free distillate dissolved in n-pentane was charged on top of the column and percolated downward through the column bed slowly. As the distillate passed through the column, the color of the attapulgus clay was changed to green indicating the

formation of neutral nitrogen compounds-ferric chloride complexes on the surface of the clay. The entrained oil was removed with 400 mls of n-pentane for 40 hours using the recycling arrangement. After removal of entrained material, the colored complexes were desorbed from the clay by eluting 1,2-dichloroethane for 70 hours. The neutral nitrogen compounds-ferric chloride complexes (colored) were dissociated while passing through the bed of anion-exchange resin. The ferric chloride salt retained on the resin while the neutral nitrogen compounds were recovered in the eluate. The neutral nitrogen compounds were recovered by removing the solvent on rotary evaporator at 40^{o}C at reduced pressure.

Separation of acids, bases and neutral nitrogen compounds was carried out for the distillate cuts from Arab Heavy and Arab Medium crude oils which were found to contain the highest amount of nitrogen compounds among the four Saudi Arabian crude oils. The acids , bases and neutral nitrogen compounds were subjected to infrared analysis which showed that similar nitrogen compound types were present in all three fractions. These compound types were identified as pyridines, pyrroles and amides. Previous studies (86) have also shown such overlapping of similar nitrogen compound types in these fractions. So it was decided to follow another scheme which separates these compounds(polar concentrate) into distinct compound types.

4.2.3 SEPARATION OF POLAR CONCENTRATE INTO NITROGEN COMPOUND TYPES BY ADSORPTION CHROMATOGRAPHY

Acids, bases and neutral nitrogen compounds were combined to form

a polar concentrate. The polar concentrate was added with 100 ml of benzene and was stirred thoroughly for 30 minutes. It was found that the polar concentrate was partially insoluble in benzene. The benzene-soluble material (nitrogen concentrate) was separated from benzene-insoluble (resins). The two materials were freed of the benzene in rotary evaporator at reduced pressure at 40°C, weighed and stored in a refrigerator. The nitrogen concentrate was fractionated into different nitrogen compound types using high performance liquid chromatography. The complete scheme is given in Figure 5.

APPARATUS AND MATERIAL

The high performance liquid chromatographic separation was performed with liquid chromatograph system Waters model 6000A equipped with a universal injector Waters model U6K and a dual wavelength absorbance detector Waters model 440. The column was of stainless steel 122 cm long and 0.8 cm in internal diameter. The packing material was neutral alumina AG7 100-200 mesh activity grade I obtained from Bio-Rad laboratories. Cyclohexane and 1,2-dichloroethane were of HPLC grade obtained from Fluka and were used as received.

PREPARATION OF COLUMN

The column was packed using the slurry method. At the time of packing, activity of the neutral alumina (grade I) was reduced to grade II by adding 3% deionised water. Slurry of the neutral alumina (grade II) was prepared in cyclohexane. The tubing was washed thoroughly several times to remove any entrained material and dried. Final washing was given with cyclohexane. The upper end of the column was fitted

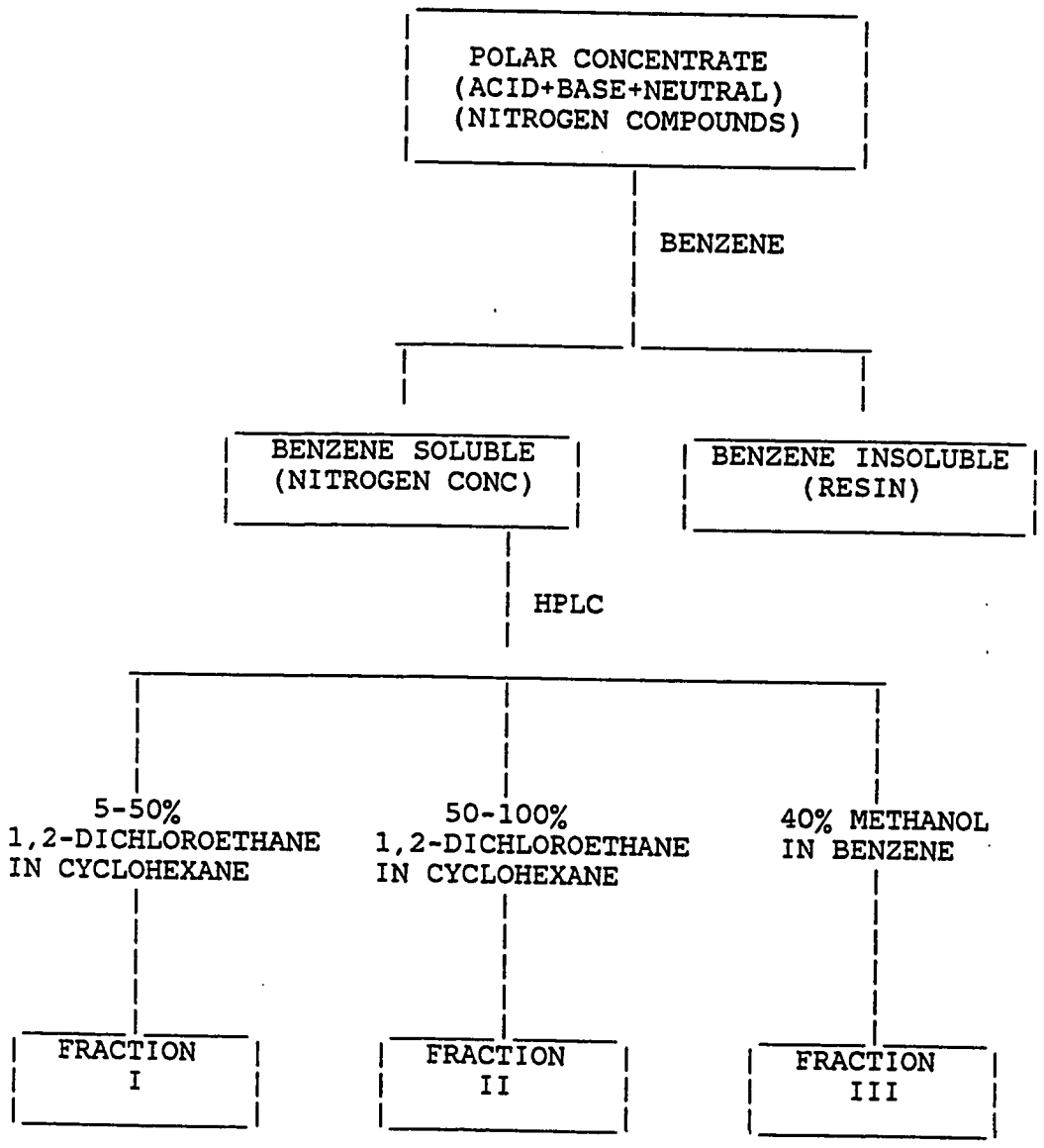


Figure 5. Scheme for the Separation of Polar Concentrate into Nitrogen Compound Types.

with a precolumn of dimension 20 cm long and 0.8 cm i.d. while the lower end was fitted with a frit to retain the packing material and to allow the solvent to pass through it. The column was initially filled with cyclohexane followed by introduction of slurry into it. The packing material was allowed to settle in the column at atmospheric pressure and ambient temperature under vibration. When the slurry was filled up to the precolumn, constant pressure was applied by solvent pump for 30 minutes to pack the material efficiently. Finally, the column was stabilized by flushing it with cyclohexane for several hours at a rate of 2 ml/minute. When the column was packed efficiently, it was attached to the system.

PROCEDURE

Nitrogen concentrate was dissolved in a mixture of cyclohexane and 1,2-dichloroethane (95:5). Six solvents were used for the separation of nitrogen concentrate into compound types. Operating conditions are given in Table 3 along with certain parameters which were calculated. The overall solvent scheme employed for all HPLC run is given in Table 4 and the solvents were eluted in the order as written. The effect of various solvents and different flow rates were evaluated on the basis of component separation. A flow rate of 2 ml/min was found suitable for separation of nitrogen concentrate into compound types. At the beginning of each day of operation, the chromatographic system was stabilized by eluting the first solvent for one hour at the flow rate used for the separation. A differential ultraviolet detector at 254nm wavelength was used to monitor the separation during the HPLC run. Each solvent was eluted for 30 minutes and the total HPLC run was

TABLE 3

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY OPERATING CONDITIONS

Instrument Used	:	Liquid Chromatograph WATERS Model 6000A, Universal Injector WATERS Model U6K, Ultraviolet Detector WATERS Model 440 and Dual Pen Chart Recorder
Column	:	Stainless Steel Tubing 122 cms long and 0.8 cm i.d.
Packing Material	:	Neutral Alumina AG7 100-200 Mesh Activity II Particle Size (112 micrometer)
Wavelength Setting	:	254 nm
Flow Rate	:	2 cm^3/min
Chart Speed	:	0.5 cm/min
Temperature	:	Ambient
Sensitivity of the Detector	:	2.0 AUFS
Average Pressure Drop	:	700 Psi
Sample Size	:	0.1 gm

TABLE 4

SOLVENT SCHEME USED FOR HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

S.NO.	SOLVENT	VOLUME CONSUMED (ml)
1.	5% 1,2-DICHLOROETHANE + 95% CYCLOHEXANE	60
2.	25% 1,2-DICHLOROETHANE + 75% CYCLOHEXANE	60
3.	50% 1,2-DICHLOROETHANE + 50% CYCLOHEXANE	60
4.	75% 1,2-DICHLOROETHANE + 25% CYCLOHEXANE	60
5.	100% 1,2-DICHLOROETHANE	60
6.	40% METHANOL + 60% BENZENE	60

completed in three hours. The last solvent was eluted until a stable base line was obtained. The column was reused after reconditioning with a sequence of less polar solvents. An automatic sample collector was used to collect the eluted components which was programmed for the collection of 5 ml portion of the eluent in test tubes. Three distinct UV absorption bands were recorded for the whole HPLC run indicating that the material was separated into three fractions. These three fractions were collected from the test tubes and were freed of the solvent in rotary evaporator at 40°C under vacuum. In this way, both Arab Heavy and Arab Medium nitrogen concentrates were fractionated into three fractions separately.

4.3 ANALYTICAL METHODS OF CHARACTERIZATION

4.3.1 ELEMENTAL ANALYSIS OF DISTILLATES

All four petroleum distillates(370-535°C) were analyzed for their carbon, hydrogen, oxygen, nitrogen and sulfur contents. The samples were analyzed for carbon, hydrogen and nitrogen using elemental analyzer model 1106 of Carlo Erba Strumentazione. Sulfur was determined using the ASTM method D129 while the oxygen was estimated by difference.

4.3.2 VAPOR PRESSURE OSMOMETRY

All four distillates(370-535°C) were subjected to average molecular weight determination. Operating conditions are given in Table 5. The average molecular weight measurement was performed on Knauer vapor pressure osmometer model 11.00 at the thermistor head temperature of

TABLE 5

VAPOR PRESSURE OSMOMETRY OPERATING CONDITIONS FOR DISTILLATES

Instrument Used	:	Vapor Pressure Osmometer(KNAUER)
Temperature of Thermistor	:	60°C
Sensitivity of Instrument	:	16.00
Response Time	:	3.0 min
Concentration of Benzil Solutions (Calibration Standard)	:	0.002, 0.005, 0.008, 0.01 Molal
Concentration of Distillate Solutions	:	15-60 gram/Kilogram

60°C using 1.0 ml hypodermic glass syringes. Benzil was used as a calibration standard for molecular weight determination. Four standard solutions of benzil were prepared in HPLC grade toluene at concentrations 0.002, 0.005, 0.008 and 0.01 Molal. Solutions of each distillate were prepared at four different concentrations in the range of 15-60 gram/kilogram of toluene. All these solutions were introduced into the osmometer and response was recorded. Four to five readings were taken for each solution and the average value was used. For both distillates and the calibration standard, the response/concentration values were plotted against the concentration separately and were extrapolated to zero concentration to obtain the value of K_{meas} and K_{cal} respectively. The ratio of the K_{cal} to K_{meas} yielded the average molecular weights of the distillates.

4.3.3 INFRARED SPECTROSCOPY

Infrared spectra were recorded for acids, bases and neutral fractions as well as for the fractions obtained from HPLC of nitrogen concentrates. Infrared spectra were recorded on grating infrared spectrophotometer model Perkin Elmer 237B. Infrared spectra for acid, base and neutral nitrogen compounds were recorded as thin film between sodium chloride plates. Infrared spectra for the six HPLC fractions were recorded quantitatively as solution in 1,2-dichloroethane in dual beam mode. The cells were made up of potassium bromide and the cell path length was 0.125 mm. The concentration of the solutions were in the range of 15-20 mg. ml^{-1}. 1,2-dichloroethane was used instead because dichloromethane tends to evaporate from the infrared cells and thus produced error in the concentration of the solutions

(71). The quantitative spectra of HPLC fractions were used to estimate the amount of different compound types present in each fraction. The compound types estimated were pyridines, pyrroles, amides, phenols and carboxylic acids. These compounds types were then classified into strong basic, weak basic and nonbasic compounds. Pyridines were considered as strong bases, amides as weak bases and the pyrroles, phenols and carboxylic acids were regarded as nonbasic compounds (40,41).

4.3.4 ULTRAVIOLET SPECTROSCOPY

Ultraviolet spectra were recorded on a ultraviolet visible spectrophotometer Perkin Elmer model 202 for all fractions. All spectra were recorded in solution of spectro grade cyclohexane using 1.0 cm path length quartz cells in dual beam mode.

4.3.5 NONAQUEOUS POTENTIOMETRIC TITRATION

Titrations were performed using Metrohm Potentiograph Model E576 in conjunction with automatic feeding unit Dosimat E575 and equipped with a calomel reference electrode and a glass indicator electrode. The titrant used was 0.05M perchloric acid prepared in reagent grade 1,4-dioxane. The titrant was prepared by diluting 4.25 mls of 70% perchloric acid to one litre of solution with dioxane. The titrant was standardized potentiometrically by primary standard grade potassium hydrogen phthalate dissolved in glacial acetic acid. The titrating medium was a mixture of acetic anhydride and benzene in the volume ratio of two to one (2:1). A number of pure nitrogen compounds were titrated in this solvent in order to achieve the following objectives.

1. To differentiate the model nitrogen compounds into strong basic, weak basic and nonbasic on the basis of their pKa values and to determine the percent titratability and basicity of these compounds in acetic anhydride:benzene (2:1) solvent.
2. To develop a relationship between the basic nitrogen present in the titrated samples and the volume of 0.05M perchloric acid solution consumed.
3. To determine the strong and weak basic nitrogen present in the distillates and HPLC fractions.

All four distillates and the fractions of nitrogen concentrate were subjected to nonaqueous potentiometric titration in order to determine the titratable bases present in these samples. All nitrogen compounds were obtained from Fluka. All titrations were performed in 100 ml beaker containing 50 ml of the solvent and a magnetic stirrer bar. The amount of model nitrogen compounds taken for titration ranged from 10-20 milligrams. The distillates were titrated in the range of 2-17 grams while the weight of HPLC fractions taken for titration was in the range 20-30 milligrams. The liquid nitrogen compounds were added to the titration solvent using a 50 microlitre microsyringe and the quantity ranged from 5-10 microlitre. While transfering the liquid nitrogen compounds, the needle of the syringe was placed beneath the surface of the solvent to prevent the evaporation of the compound being added. The overall potentiometric titration conditions are given in Table 6.

4.3.6 GAS CHROMATOGRAPHY

The fractions obtained from HPLC separation were subjected to gas

TABLE 6

NONAQUEOUS POTENTIOMETRIC TITRATION CONDITIONS

Instrument	:	Potentiograph Metrohm Model E576 Dosimat Metrohm Model E575
Electrodes	:	Calomel and Glass Electrodes
Titrant	:	0.05M Perchloric Acid in Dioxane
Primary Standard	: :	Potassium Hydrogen Phthalate in Glacial Acetic Acid
Solvent	:	Acetic Anhydride : Benzene(2:1)
Temperature	:	Ambient
Response Time	:	< 1 Second

chromatographic analysis using a selective thermionic detector called Nitrogen Phosphorus Detector(NPD).

APPARATUS AND MATERIALS

The gas chromatograph was Varian 3700 equipped with nitrogen phosphorus detector (NPD) and a 1 mv recorder from Varian model 9176. The column was 2 meter long, 3 mm o.d. and 2 mm i.d. made of stainless steel tubing packed with 10% OV-101 on 80-100 mesh chromosorb W-HP. All model nitrogen compounds were of highest available purity obtained from Fluka. All standard and sample solutions were made in reagent grade 1,2-dichloroethane obtained from Fluka which was flash distilled. Naphthalene was obtained from BDH Laboratories.

PROCEDURE

The overall gas chromatographic operating conditions are given in Table 7. A hydrogen flow rate of 3.5 cm^3/min was found optimum for maximum sensitivity without sacrificing selectivity. To compensate for loss in sensitivity due to aging of the bead, incremental adjustments were made, as appropriate in the bead current.

The effects of different carrier gases and their flow rates on the detector background current were determined. Different isothermal and programmed temperatures were employed depending on the boiling range of the sample and the separation desired. Isothermal column temperatures were in the range of 100-200^{o}C. For temperature programmed runs, the sample was charged to the column at 80^{o}C and

TABLE 7

GAS CHROMATOGRAPHY OPERATING CONDITIONS FOR HPLC FRACTIONS

Instrument Used	:	Gas Chromatograph Varian Model 3700
Detector	:	Nitrogen Phosphorus Detector (NPD)
Recorder	:	Varian Model 9176
Column	:	Stainless Steel Tubing 2 m long , 3 mm o.d. and 2 mm i.d.
Packing Material	:	10% OV-101 Supported on 80-100 mesh Chromosorb W-HP
Flow Rates(cm^3/min)		
Air	:	175
Hydrogen	:	3.5
Helium(Carrier)	:	30
Temperatures(^oC)		
Injector	:	270
Detector	:	350
Column	:	100-200(Isothermal)
	:	80 + 4^oC/min - 280 (Programming)
Injection Volume	:	1.0 microlitre
Bead Voltage	:	4.0 Volt
Bead Heating Current	:	4.0 Ampere
Chart Speed	:	0.25 cm/min.
Selectivity(gC/gN)	:	19668
Background Current	:	5 Picoampere

after 4 minutes, programming was initiated at the rate of 4°C/min and was continued to a maximum of 280°C. Elution was continued at the maximum temperature, if necessary, until the completion of the chromatogram.

At the beginning of each day of operation, the chromatographic system was conditioned by heating the column to an elevated temperature of 200°C and while at that temperature, charging at least two successive 1 microlitre injections of a solution containing 25 ppm nitrogen as quinoline in 1,2-dichloroethane. Subsequently, the column temperature was readjusted as required for calibration and analysis.

The calibration of the chromatographic system was done with a reference solution containing 25 ppm of quinoline which correspond to 2.71 ppm nitrogen and 17400 ppm of naphthalene which correspond to 16300 ppm carbon. The composition of this solution was chosen to represent a reasonable test both for selectivity and sensitivity. The relative peaks areas obtained for quinoline and naphthalene were 3.27 and 1.00 respectively.

Selectivity of the detector was calculated by the expression

$$\text{Selectivity} = \frac{A_1 \times W_2}{A_2 \times W_1}$$

where

A_1 = area response to quinoline

A_2 = area response to naphthalene

W_1 = grams of nitrogen as quinoline

W_2 = grams of carbon as naphthalene

Using this expression, the selectivity of the detector was calculated to be 1.97×10^4 grams of carbon per gram of nitrogen (gC/gN) present in the mixture. During all gas chromatographic runs, carbon to nitrogen (gC/gN) selectivity of at least 1.50×10^4 was maintained.

Calibration was made, following conditioning of the column, at an isothermal temperature generally in the range of 100-150°C with a sample size of 1 microlitre. The solutions of model nitrogen compounds were prepared in the concentration range of 20-50 ppm in 1,2-dichloroethane. The solutions of pure nitrogen compounds were injected individually in order to find their retention times. For each model compound, minimum two injections were made in order to confirm its response and retention time. In order to demonstrate the efficiency of the column, a synthetic mixture was prepared which contained 0.32-1.48 ppm of 9 model nitrogen compounds. The composition of this solution is given in Table 8. The samples of HPLC fractions were prepared in the same solvent and injected under identical conditions.

In general, the NPD bead voltage was such that the system background or bead current was not greater than 30 picoampere. With well conditioned columns, the background current was 5 picoampere or even less.

4.3.7 GAS CHROMATOGRAPHY-MASS SPECTROMETRY

Fractions obtained from high performance liquid chromatography of

TABLE 8

COMPOSITION OF A SYNTHETIC MIXTURE OF MODEL NITROGEN COMPOUNDS

NITROGEN COMPOUNDS	CONCENTRATION ngm/microlitre
1-METHYLPYRROLE	0.32
PYRROLIDINE	0.93
QUINOLINE	0.98
INDOLE	0.72
1,2,3,4-TETRA HYDROQUINOLINE	0.70
PHENAZINE	0.74
CAFFEINE	1.48
ACRIDINE	0.96
IMIDAZOLE	0.49

nitrogen concentrate were analyzed by gas chromatographic-mass spectrometric technique. The GC-MS system was quadruple type Model R-10-10 from Nermag in combination with Riber 400 data acquisition system. The gas chromatograph was single column model 31 from Girdle Inc. equipped with a built-in linear temperature programmer, solvent diversion system and sample splitter. Gas chromatograph was equipped with a capillary column. Other operating conditions of GC-MS are given in Table 9.

4.3.8 MASS SPECTROMETRY

The resin materials (benzene-insoluble) obtained from the polar concentrate of both Arab Heavy and Arab Medium distillates were subjected to mass spectral analysis. The operating conditions are given in Table 10.

TABLE 9

GAS CHROMATOGRAPHY-MASS SPECTROMETRY OPERATING CONDITIONS FOR HPLC FRACTIONS

Instrument Used	:	Mass Spectrometer Model R-10-10(NERMAG) Quadruple Type with Riber 400 Data Acquisition System and Single Column Gas Chromatograph
Column	:	FFAP WCOT Fused Silica Capillary Column 50 m long, 0.33 mm o.d., 0.22 mm i.d.
Carrier Gas	:	Helium
Flow Rate	:	2 cm^3/min
Temperatures(^oC)		
Injection Port	:	220
Interface	:	230
Oven	:	150 + 5^oC/min - 220 (Programming)
Injection Volume	:	1.0 microlitre
Electron Energy	:	70 Electron Volts
Filament Current	:	0.22 milliampere
Mass Range used	:	60-340 amu

TABLE 10

MASS SPECTROMETRY OPERATING CONDITIONS FOR RESIN MATERIALS

Instrument Used	:	Mass Spectrometer Model JMS-HX100(JEOL) Direct Inlet Probe-Electron Impact
Temperature	:	100-280°C 128°C/min (Programming)
Electron Energy	:	70 Electron Volts
Filament Current	:	0.1 milliampere
Mass Range used	:	1-270 amu

CHAPTER 5

RESULTS AND DISCUSSION

5.1 GENERAL CHARACTERISTICS OF SAUDI ARABIAN CRUDE OILS

The crude oils were obtained from ARAMCO and were stored in non-corrosive containers at low temperature(20°C) to avoid formation of artifacts. For the preliminary study, the following four crude oils were employed which are marketed by Saudi Arabia. The first two of the four crude oils were examined in detail.

1. Arab Heavy (AH)

2. Arab Medium (AM)

3. Arab Light (AL)

4. Arab Berri (AB)

These crude oils are from different sources and have characteristics properties.

Arab Heavy is obtained from an offshore oil field, Safaniya, which is located about 125 miles northwest of the exporting terminal of Ras Tanura. Safaniya is the largest offshore oil field in the world. Arab Heavy is a medium gravity paraffinic crude oil.

Arab Medium is a medium gravity, paraffinic wax-containing crude oil. It is produced as multistage separated oil from a blend of Abu Safah, Khursaniyah and Qatif oil fields, all located onshore near exporting terminal of Ras Tanura.

Arab Light is a medium paraffinic, moderately high gravity crude oil. It is a blend of such fields as Abqaiq, Ain Dar, Shedgum, Uthmaniya, Fadhili, Abu Hadriya, Hawiyah and Qatif. These fields are located in the northeast of Saudi Arabia.

Arab Berri (Extra Light) is a high gravity paraffinic crude oil. It is produced from Berri oil field.

Table 11 summarizes general properties of all four Saudi Arabian crude oils. These crude oils represent a broad range of crude types. Arab Heavy is the heaviest while Arab Berri is the lightest of all four crude oils. The API gravity of Arab Heavy is lower while that of Arab Berri is higher and there is a gradual increase in API gravity from Arab Heavy (27.90) to Arab Berri (37.80) through Arab Medium (30.36) and Arab Light (33.45) crude oils. This trend in API gravity is accompanied by a decrease in their nitrogen and sulfur contents. The percent sulfur and percent nitrogen contents range from 2.67-1.20% and 0.168-0.042% respectively for the four crude oils.

5.2 PREPARATION OF HIGH-BOILING DISTILLATES (370-535^{o}C)

The wiped-film still used to prepare fractions by distillation can remove high-boiling materials without causing measurable decomposition. An important characteristic of the still is that it provides a short residence time for the sample in the heated zone, thereby minimizing thermal exposure of any labile compounds. This has been demonstrated repeatedly since, in no case, has there been any indication of gas formation or property change while taking materials boiling up to 535^{o}C or above. A good agreement is noted between the boiling points

TABLE 11

GENERAL PROPERTIES OF SAUDI ARABIAN CRUDE OILS

PROPERTIES	ASTM METHOD	ARAB HEAVY	ARAB MEDIUM	ARAB LIGHT	ARAB BERRI
Color	Visual	Black	Black	Black	Black
Gravity, ^{o}API	D287	27.90	30.36	33.45	37.86
Gravity, Specific (60/60^{o}F)	D287	0.8875	0.8740	0.8575	0.8355
Viscosity SUS 100^{o}F(37.8^{o}C)	D445	118	71	49	41
Pour Point ^{o}F(^{o}C)	D97	-10(-23.2)	+10(-12.2)	+5(-15.0)	0(-17.8)
Nitrogen Weight Percent	-	0.168	0.114	0.098	0.042
Sulfur Weight Percent	D129	2.67	2.45	1.98	1.20

indicated by pressure-temperature relationship in the still and the simulated distillation data obtained by gas chromatographic simulation. Excellent separation by boiling range was achieved by the use of the still. However, careful control of temperature, pressure, feed rate, limited thermal exposure and a uniform thin film for evaporation are essential for acceptable and reproducible results.

5.3 BOILING RANGE DISTRIBUTION OF DISTILLATES DETERMINED BY SIMULATED DISTILLATION

The Arab Heavy and Arab Medium distillates were subjected to simulated distillation in order to determine the boiling range distribution of the distillates. This was accomplished by temperature programmed gas liquid chromatography under the ASTM method D2887-73. It provides a measure of the boiling range of the material and the distribution of the normal paraffins therein. Figures 6 and 7 illustrate the chromatographic curves obtained for distillate (370-535^{o}C) from Arab Heavy and Arab Medium crude oils respectively. The sharp peaks appeared in the chromatogram are due mostly to normal paraffins. The Arab Heavy distillate show less prominent and few peaks as compared to Arab Medium distillate. This may be due to the low paraffinic contents and greater aromaticity of Arab Heavy as compared to Arab Medium distillate. The simulated distillation data shows that the separation of distillates (370-535^{o}C) using wiped-film molecular still is quite good.

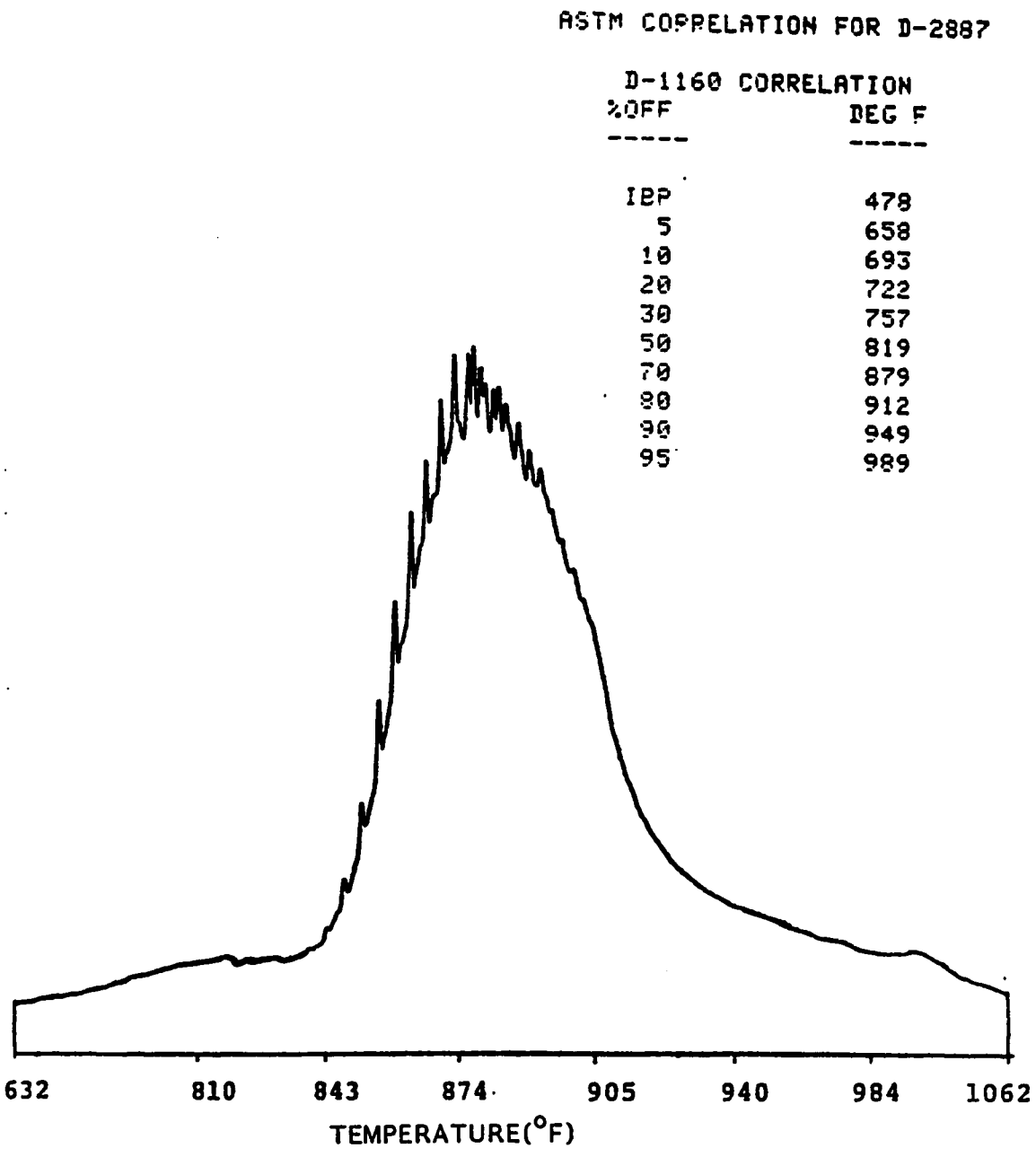


Figure 6. Simulated Distillation Curve for Arab Heavy Distillate Produced by Gas Chromatography

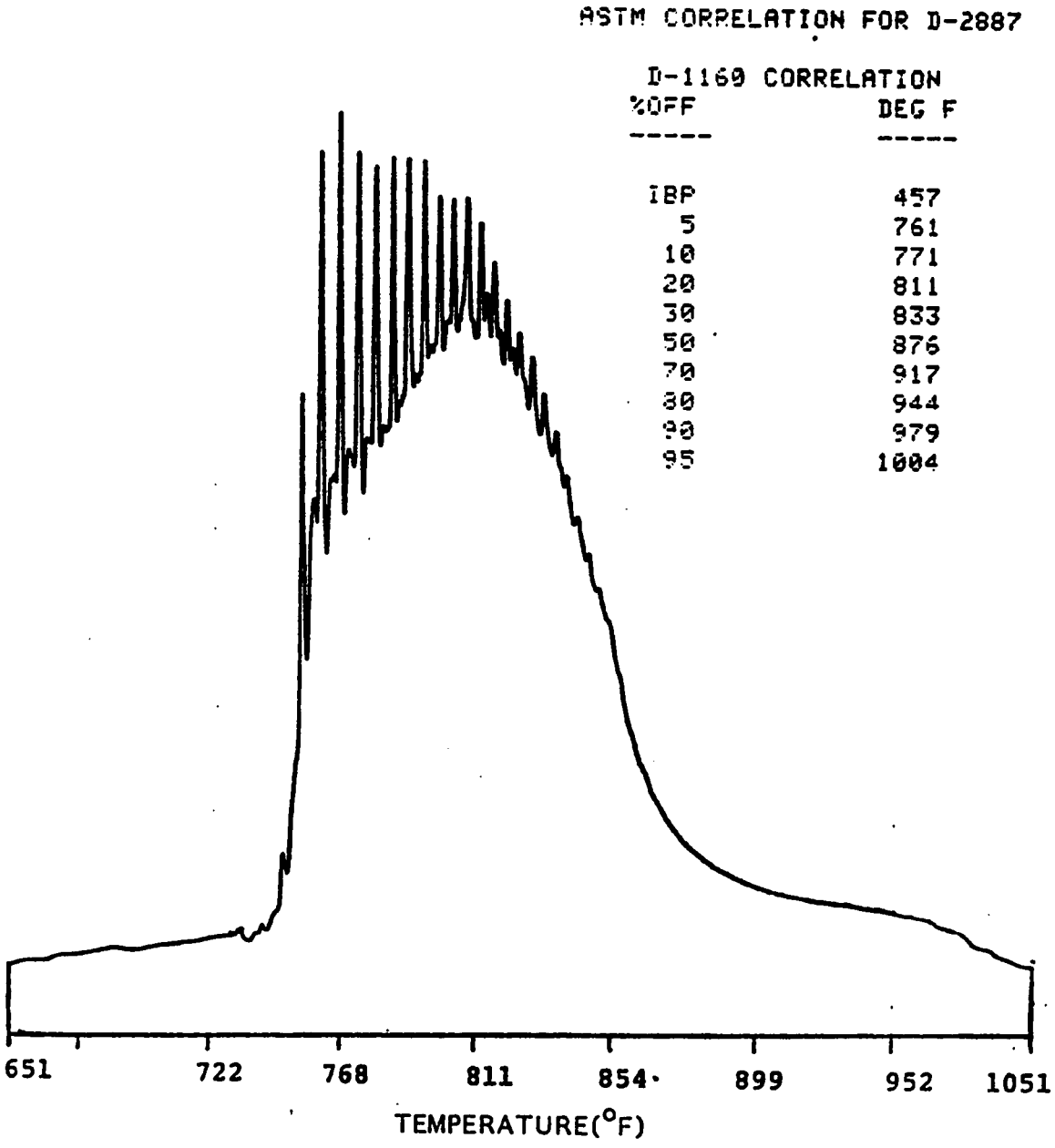


Figure 7. Simulated Distillation Curve for Arab Medium Distillate Produced by Gas Chromatography

5.4 CHARACTERIZATION OF HIGH-BOILING PETROLEUM DISTILLATES (370-535°C)

The distillate cuts (370-535°C) obtained from four crude oils were analyzed for their various properties and compositions. These properties include gravity, carbon residue, weight percent elemental composition and basicity.

5.4.1 GENERAL CHARACTERISTICS OF HIGH-BOILING DISTILLATES (370-535°C)

The general chemical and physical properties of the distillates were determined. These properties which are given in Table 12 show an increase in the API gravity, aniline point and weight percent yields and a decrease in refractive index, carbon residue and viscosity from Arab Heavy to Arab Berri through Arab Medium and Arab Light distillates.

It is generally recognized that increased amount of aromatic compounds in a material results in an increase in specific gravity(low API) whereas increase in aliphatic compounds decreases the specific gravity (high API). Therefore, Arab Heavy distillate contains more aromatics while the other distillates contain more aliphatic compounds.

The refractive index is a relative measure of hydrocarbon composition of the material. High value of refractive index indicates the presence of aromatic compounds whereas the low value suggest a paraffinic material comparatively. So Arab Heavy distillate contains more aromatics as compared to other distillates.

TABLE 12

GENERAL PROPERTIES OF HIGH-BOILING DISTILLATES

(370-535°C) FROM SAUDI ARABIAN CRUDE OILS

PROPERTIES	ASTM METHOD	ARAB HEAVY	ARAB MEDIUM	ARAB LIGHT	ARAB BERRI
Color	Visual	Dark Brown	Moderate Brown	Brown	Brown
Yield on crude Weight Percent	-	22.7	23.2	23.3	23.6
Gravity, °API	D287	20.29	20.41	21.83	23.92
Gravity, Specific (60/60°F)	D1298	0.9325	0.9320	0.9225	0.9100
Refractive Index at 67°C	D1218	1.51027	1.50123	1.49249	1.48195
Viscosity at 210 °F (98.9°C), cSt	D445	7.0	6.6	5.9	5.5
Carbon Residue, Weight %	D189	0.15	0.12	0.10	0.05
Aniline Point, °F(°C)	D611	167(75)	173(78)	185(85)	194(90)
Pour Point, °F(°C)	D97	+95(35)	+85(29)	+80(27)	+80(27)

The aniline point is a measure of presence of aromatic compounds. Most of the aromatic compounds are soluble in aniline. The aniline point is lowest for Arab Heavy distillate than the rest of the three distillates. This may be attributed to high aromaticity of Arab Heavy distillate. The weight percent yield of distillates increases from Arab Heavy to Arab Berri because Arab Heavy contains more high-boiling compounds than Arab Berri distillate.

Viscosity is the most important single fluid characteristic governing the motion of petroleum and petroleum products and it is usually a measure of the internal resistance to motion of a fluid by reason of the forces of cohesion between molecules or molecular groupings. Higher values of viscosity refers to more viscous material and thus Arab Heavy distillate contains larger molecules compared to other three distillates. The relatively high viscosity and carbon residue for Arab Heavy distillate further support the increased aromaticity of Arab Heavy distillate. Thus it appears that as we go from Arab Heavy to Arab Berri through Arab Medium and Arab Light, the paraffinicity of the distillates gradually increases and the aromaticity gradually decreases. The color of the Arab Heavy distillate is darker than the rest of the distillates and the intensity of the color decreases from Arab Heavy to Arab Berri distillate.

5.4.2 ELEMENTAL ANALYSIS OF THE DISTILLATES(370-535^{O}C)

The elemental composition of all four distillates determined in terms of weight percent hydrogen, carbon, nitrogen, oxygen and sulfur is given in Table 13. Among these distillates, the weight percent carbon,

TABLE 13

ELEMENTAL COMPOSITION OF THE DISTILLATES(370-535^{O}C)

	WEIGHT PERCENT OF DISTILLATE				
DISTILLATE	HYDROGEN	CARBON	NITROGEN	OXYGEN	SULFUR
ARAB HEAVY	11.06	85.37	0.098	0.692	2.78
ARAB MEDIUM	11.29	85.28	0.084	0.656	2.69
ARAB LIGHT	11.66	85.19	0.067	0.593	2.49
ARAB BERRI	11.98	85.07	0.055	0.535	2.36

nitrogen, oxygen and sulfur decreases while hydrogen increases from Arab Heavy to Arab Berri through Arab Medium and Arab Light distillates. In each distillate, the trend of weight percent for these elements is

Carbon > Hydrogen > Sulfur > Oxygen > Nitrogen

From the elemental weight percent, the empirical formulae of the distillates were calculated which are given in Table 14. For calculating empirical formulae, the weight percent of each element was divided by its atomic weight. For each distillate, the figures obtained were divided by the least value. As a result, the relative number of atoms of each element were found. Table 15 list the atomic ratios of various elements present in the distillates.

The nitrogen-to-carbon (N/C) atomic ratio of distillates decreases from Arab Heavy (0.00097) to Arab Berri (0.00054) through Arab Medium (0.00086) and Arab Light (0.00067). The N/C ratio provides information about relative basic functionalities present in the distillates. This is because in petroleum, most of the nitrogen present is in the form of basic nitrogen compounds such as pyridines and amides. In case of high nitrogen contents, the N/C ratio increases and the distillate become more basic in nature. The Arab Heavy which posseses relatively higher N/C ratio is expected to have stronger basic properties as compared to Arab Medium and Arab Light distillates. On the other hand, Arab Berri has lowest N/C ratio and thus has weakest basic properties compared to other three distillates. The higher basicity of Arab Heavy distillate is also exhibited by higher N/O atomic

TABLE 14

EMPIRICAL FORMULA OF THE DISTILLATES(370-535^{O}C)

DISTILLATE	EMPIRICAL FORMULA
ARAB HEAVY	$C_{32}\ H_{49}\ N_{0.031}\ O_{0.19}\ S_{0.39}$
ARAB MEDIUM	$C_{29}\ H_{46}\ N_{0.025}\ O_{0.17}\ S_{0.35}$
ARAB LIGHT	$C_{27}\ H_{44}\ N_{0.018}\ O_{0.14}\ S_{0.30}$
ARAB BERRI	$C_{26}\ H_{43}\ N_{0.014}\ O_{0.12}\ S_{0.27}$

TABLE 15

ATOMIC RATIO OF DIFFERENT ELEMENTS PRESENT IN THE DISTILLATES

DISTILLATE	N/O	N/C	H/C	O/C
ARAB HEAVY	0.16	0.00097	1.54	0.0060
ARAB MEDIUM	0.15	0.00086	1.60	0.0059
ARAB LIGHT	0.13	0.00067	1.64	0.0052
ARAB BERRI	0.12	0.00054	1.70	0.0046

ratio.

The nitrogen-to-oxygen (N/O) atomic ratio of distillates decrease from Arab Heavy (0.16) to Arab Berri (0.12) through Arab Medium (0.15) and Arab Light (0.13). The N/O ratio is a measure of relative basicity of the material. This may be due to the reason that oxygen is mainly present as acidic functionalities such as phenols and carboxylic acids whereas most of the nitrogen occurs as basic compounds. A higher oxygen or lower nitrogen contents of the distillate results in lower N/O ratio and exhibit lower basicity whereas a lower oxygen or higher nitrogen lead to higher N/O ratio and indicates higher basicity of the sample. Thus Arab Heavy distillate is more basic than Arab Berri.

The hydrogen-to-carbon (H/C) atomic ratio increases from Arab Heavy (1.54) to Arab Berri (1.70) through Arab Medium (1.60) and Arab Light (1.64) distillates. The H/C ratio of crude and its fractions have a great significance. A high H/C ratio indicates the presence of long chain aliphatic compounds while a low H/C ratio indicates the predominance of aromatic ring structure. The alkanes have higher H/C ratio than aromatics. Methane is the hydrocarbon with smallest mass and has the highest H/C ratio of four. On the other hand, the highly condensed polyaromatics with higher molar masses have the smallest H/C ratio which approaches zero as the number of rings increases. The H/C ratio is a measure for degree of ring condensation regardless of whether the rings are aromatic or naphthenic in character (130) and it is indicative of comparative amount of aliphatics and aromatics present. In general, the lower the H/C ratio, the higher the degree of ring

condensation. These results show that the aromaticity characteristics of the distillates gradually decreases from Arab Heavy to Arab Berri through Arab Medium and Arab Light distillates. Thus Arab Heavy has higher degree of condensation i.e. greater average molecular size than other three crude distillates.

The oxygen-to-carbon (O/C) atomic ratio decreases from Arab Heavy (0.0060) to Arab Berri (0.0046) through Arab Medium (0.0059) and Arab Light (0.0052) distillates. This decrease in O/C ratio indicates that overall oxygen functional groups are highest in Arab Heavy and lowest in Arab Berri.

Higher N/C and O/C ratio and lower H/C ratio for Arab Heavy distillate suggest more aromatic and more polar characteristics as compared to other three distillates. Thus the aromaticity and polarity of the distillates decrease from Arab Heavy to Arab Berri.

5.4.3 MOLECULAR WEIGHT OF THE DISTILLATES(370-535^{O}C)

The average molecular weights of distillates determined by vapor pressure osmometry are shown in Table 16. The values of average molecular weights decrease from Arab Heavy (445) to Arab Berri (365) through Arab Medium (411) and Arab Light (383) distillates. This decrease in molecular weight is in line with a similar decrease in the specific gravities, viscosities and carbon residues (Table 12) for these four Arab crude distillates. These results suggest that the concentration of high molecular weight compounds is higher in Arab Heavy and decreases from Arab Heavy to Arab Berri. The Arab Medium and Arab Light distillates lies in between.

TABLE 16

MOLECULAR WEIGHT OF THE DISTILLATES DETERMINED BY VAPOR PRESSURE OSMOMETRY

DISTILLATE	MOLECULAR WEIGHT
ARAB HEAVY	445
ARAB MEDIUM	411
ARAB LIGHT	383
ARAB BERRI	365

5.4.4 NONAQUEOUS POTENTIOMETRIC TITRATION

Nonaqueous potentiometric titration was used to study basic and nonbasic functionalities present in different petroleum samples of four crude oils. The purpose was to determine the amount of basic and nonbasic nitrogen present in the distillate as well as in HPLC fractions. Model nitrogen compounds were titrated under the similar conditions to differentiate them into strong, weak and nonbasic species.

5.4.4.1 CLASSIFICATION OF MODEL NITROGEN COMPOUNDS

A number of model nitrogen compounds were titrated potentiometrically in order to determine their titratability in a mixture of acetic anhydride and benzene(2:1) using perchloric acid in dioxane as a titrant. The titrant was standardized by the potentiometric titration with primary standard grade potassium hydrogen phthalate dissolved in glacial acetic acid. The results are listed in Table 17 along with their pKa values in water and percentage purity. These nitrogen compounds were classified into three classes on the basis of their pKa values (104).

1. Strong Bases(pKa > 2)

This class comprises of compounds having pKa values greater than 2. It includes pyridine and its benzologs like acridines, phenanthridines and quinolines, imidazole, pyrrolidine and aromatic and aliphatic amines(104). This class also contains saturated and alkyl substituted derivatives of these compounds.

TABLE 17

PERCENT TITRATABILITY AND BASICITY OF MODEL NITROGEN COMPOUNDS DETERMINED BY NONAQUEOUS POTENTIOMETRIC TITRATION

COMPOUND	pKa	% TITRATED	% PURITY	BASICITY
PYRROLIDINE	11.27	100	99	S
IMIDAZOLE	6.95	98	99	S
ACRIDINE	5.58	100	98	S
PYRIDINE	5.25	99	99	S
1,2,3,4-TETRA HYDROQUINOLINE	5.03	99	97	S
QUINOLINE	4.81	99	99	S
PHENANTHRIDINE	4.48	100	98	S
PHENAZINE	1.30	100	98	W
CAFFEINE	0.61	97	96	W
ACETAMIDE	-0.48	98	98	W
ACETANILIDE	-1.00	100	99	W
1-METHYL INDOLE	-1.80	96	97	W
INDOLE	-2.90	NT	98	N
1-METHYL PYRROLE	-2.90	NT	98	N
PYRROLE	-3.80	NT	98	N
CARBAZOLE	-	NT	97	N

NT=NONTITRATABLE; S=STRONG BASE; W=WEAK BASE; N=NONBASIC

2. Weak Bases(-2 < pKa < 2)

This class consists of nitrogen compounds having pKa values less than 2 and greater than -2. It includes compounds like acetamide, acetanilide and caffeine. It also includes diaza compounds like phenazine and pyrrolic compounds like 1-methylindole. Most of the nitrogen compounds which appear as weak bases in acetic anhydride are aliphatic and aromatic amide types(98,105).

3. Nonbasic(Nontitratable) Nitrogen Compounds(pKa < -2)

This class consists of nitrogen compounds having pKa values less than -2. This class includes pyrrole, 1-methylpyrrole, indole, and carbazole. These compounds were nontitratable in this solvent system and were nonbasic in nature (104). Most of the pyrrolic compounds were found nontitratable in this solvent.

5.4.4.2 RELATIONSHIP BETWEEN THE AMOUNT OF BASIC NITROGEN AND THE VOLUME OF PERCHLORIC ACID CONSUMED FOR TITRATION

A relationship was developed between the amount of basic nitrogen present and the volume of standard perchloric acid solution consumed. The perchloric acid was 0.05M prepared in dioxane. The results are tabulated in Table 18 and the plot obtained is shown in Figure 8. The slope of the plot was calculated using least square fit and found to be 0.717 which means that there is 0.717 milligram of basic nitrogen present in the sample for every millilitre of 0.05M perchloric acid

TABLE 18

NONAQUEOUS POTENTIOMETRIC TITRATION OF MODEL NITROGEN COMPOUNDS

COMPOUND	WEIGHT OF SAMPLE (mg)	TOTAL NITROGEN PRESENT (mg)	PERCHLORIC ACID CONSUMED (ml)	MOLECULAR WEIGHT OF COMPOUNDS
ACRIDINE	17.17130	1.34	1.91	179.22
PHENANTHRIDINE	18.14374	1.41	2.01	179.22
QUINOLINE	14.98461	1.62	2.27	129.16
PYRROLIDINE	10.93201	2.15	3.00	71.12
PYRIDINE	13.63400	2.41	3.42	79.11

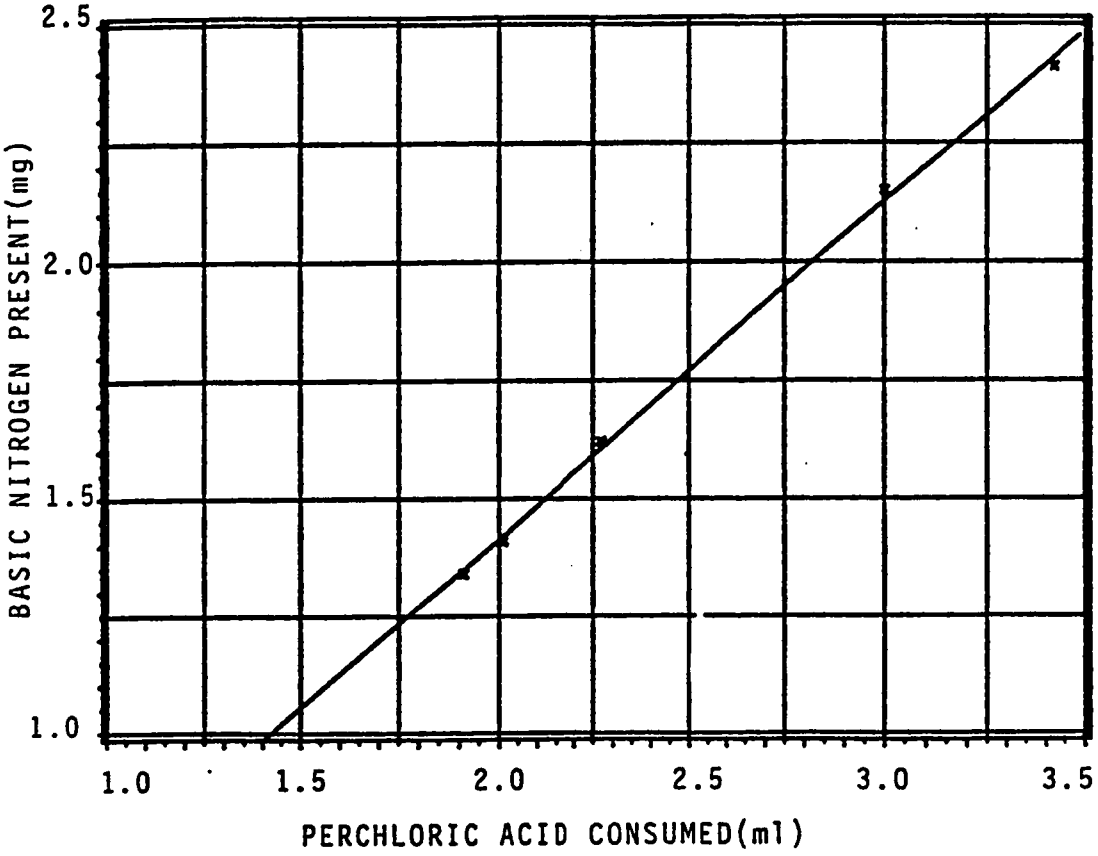


Figure 8. The Plot of Milligrams of Basic Nitrogen Present in Model Nitrogen Compounds vs. millilitres of 0.05M Perchloric Acid Consumed for Titration. The Slope of the Straight Line is 0.717.

consumed. This relationship was developed for determining basic nitrogen compounds in high-boiling distillates and other fractions.

5.4.4.3 NONAQUEOUS POTENTIOMETRIC TITRATION OF DISTILLATES (370-535°C)

All four high-boiling petroleum distillates were subjected to nonaqueous potentiometric titration in order to determine the amount of basic nitrogen present. The titration curves are shown in Figure 9. All four distillates exhibited well defined titration curves with two distinct inflections. The first inflection was very sharp and appeared because of the presence of strong basic nitrogen compounds present in the distillates. The second inflection was due to the presence of weak basic nitrogen compounds.

Basic nitrogen was calculated in terms of the weight percent of the sample titrated using the slope of the plot of Figure 8 which is 0.717. The expression used for the calculation of weight percent basic nitrogen is given below.

$$\text{Weight \% Basic Nitrogen} = \frac{\text{Millilitres of Acid Consumed} \times \text{Slope} \times 100}{\text{Milligrams of Sample taken}}$$

The results are given in Table 19. It was observed that the weight percent of total basic compounds decreases from Arab Heavy (0.075) to Arab Berri (0.018) through Arab Medium (0.049) and Arab Light (0.032) distillates. The weight percent basic nitrogen present in the Arab Berri is in fact less than one-fourth of the basic nitrogen present

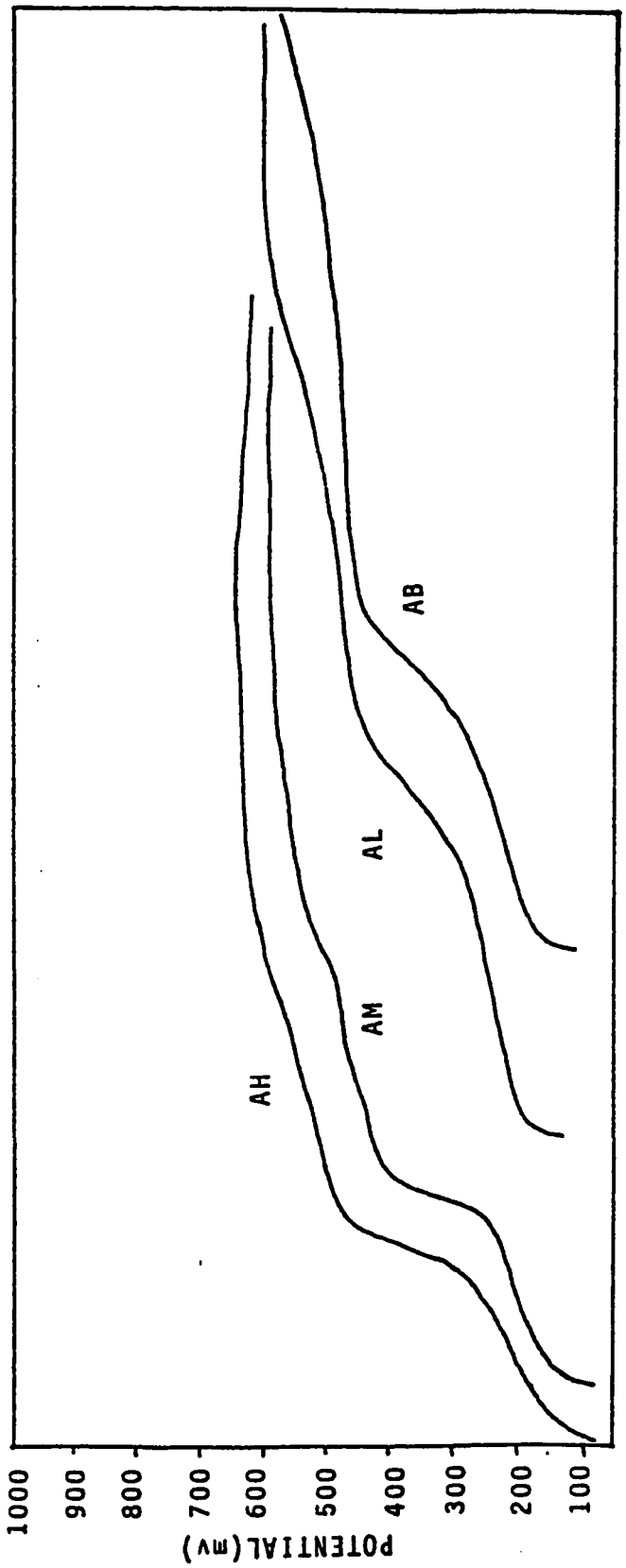


Figure 9. Nonaqueous Potentiometric Titration Curves obtained for Arab Heavy(AH), Arab Medium(AM), Arab Light(AL) and Arab Berri(AB) High-Boiling Distillates (370-535°C) of Saudi Arabian Crude Oils

TABLE 19

PERCENT BASIC NITROGEN PRESENT IN THE DISTILLATES AS DETERMINED BY NONAQUEOUS POTENTIOMETRIC TITRATION

DISTILLATE	WEIGHT OF SAMPLE (gm)	PERCHLORIC ACID CONSUMED (ml)	PERCENT BASIC NITROGEN CALCULATED
ARAB HEAVY	2.04343	2.14	0.075
ARAB MEDIUM	3.33852	2.28	0.049
ARAB LIGHT	6.38350	2.85	0.032
ARAB BERRI	16.74310	4.21	0.018

in Arab Heavy. The Arab Light also contains very little basic nitrogen. Nitrogen types as total basic, strong basic, weak basic and nonbasic nitrogen present in the distillates are shown in Table 20. The total nitrogen obtained from elemental analysis is also reported in Table 20. The difference of total basic nitrogen and total nitrogen is reported as nonbasic nitrogen. Basic and nonbasic nitrogen as weight percent of the total nitrogen present are also reported in Table 20. These results are also shown in the form of bar graph in Figure 10. These results show that the basicity of the distillates decreases from Arab Heavy to Arab Berri through Arab Medium and Arab Light.

5.5 CORRELATION OF ELEMENTAL ANALYSIS, MOLECULAR WEIGHT AND THE POTENTIOMETRIC TITRATION RESULTS OBTAINED FOR HIGH-BOILING DISTILLATES (370-535^{o}C)

The distillates (370-535^{o}C) obtained from four Saudi Arabian crude oils were analyzed for their various chemical and physical properties. The elemental analysis showed that the weight percent nitrogen decreases from Arab Heavy to Arab Berri through Arab Medium and Arab Light distillates. The data indicates that the weight percent nitrogen present in Arab Berri is about one-third of that present in Arab Heavy and one-half of that present in Arab Medium. The atomic ratios of nitrogen with other elements suggest that the polarity and basicity of these distillates decrease from Arab Heavy to Arab Berri. This trend in basicity is also observed by the titration data. The titration data indicates that there is a gradual decrease of basicity from Arab Heavy to Arab Berri distillate. The titration data shows that in Arab Berri, the weight percent basic nitrogen is even less than one-

TABLE 20

DISTRIBUTION OF TOTAL NITROGEN PRESENT IN THE DISTILLATES

AS PERCENT STRONG BASIC, WEAK BASIC AND NONBASIC TYPE

	WEIGHT PERCENT OF DISTILLATE					WEIGHT PERCENT OF TOTAL NITROGEN			
DISTILLATE	TOTAL NITROGEN	TOTAL BASIC	STRONG BASIC	WEAK BASIC	NONBASIC NITROGEN	TOTAL BASIC	STRONG BASIC	WEAK BASIC	NONBASIC NITROGEN
ARAB HEAVY	0.098	0.075	0.041	0.034	0.023	77	42	35	23
ARAB MEDIUM	0.084	0.049	0.023	0.026	0.035	58	27	31	42
ARAB LIGHT	0.067	0.032	0.014	0.018	0.035	48	21	27	52
ARAB BERRI	0.039	0.018	0.008	0.010	0.021	46	20	26	54

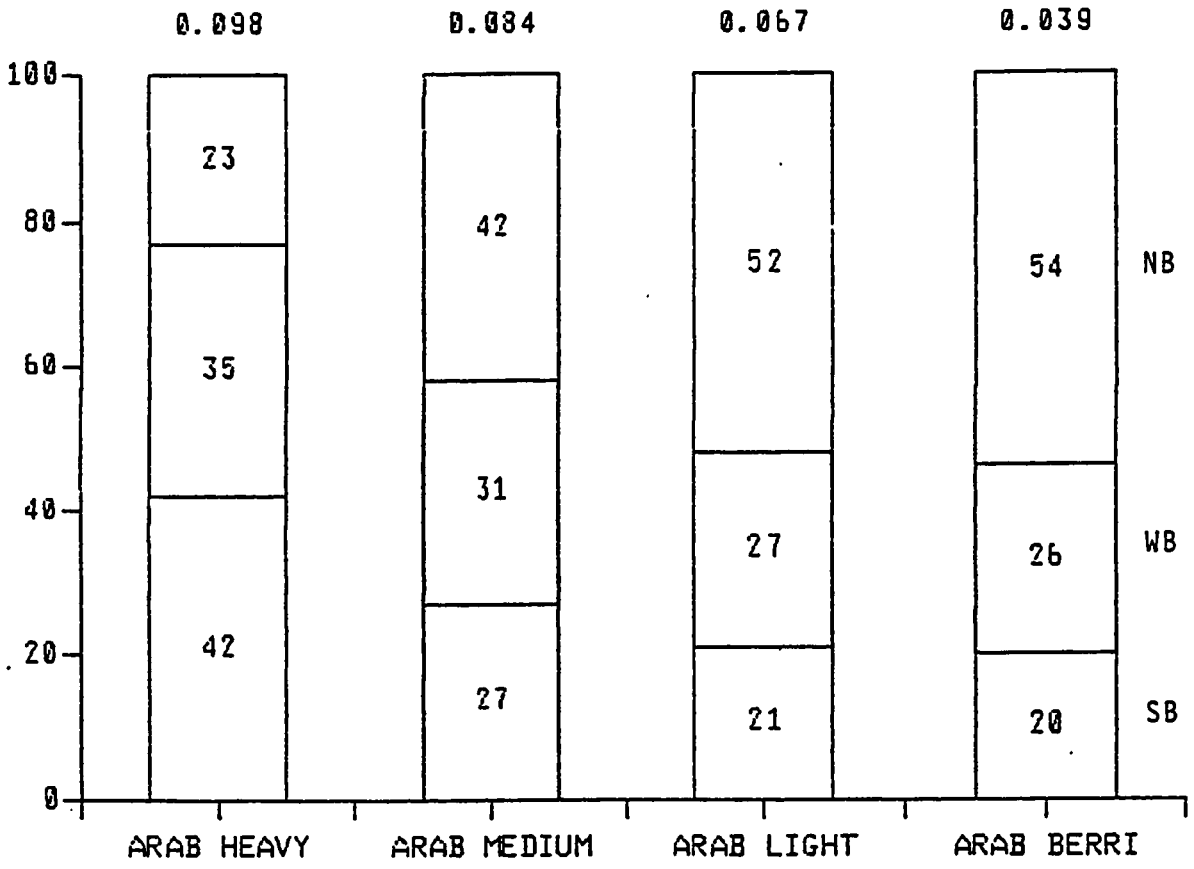


Figure 10. Bar Graph showing the Distribution of Total Nitrogen Present in the Distillates as Strong Basic (SB), Weak Basic(WB) and Nonbasic Type(NB) in terms of Weight Percent of the Total Nitrogen. The values given above the Bars are the Weight Percent of Total Nitrogen Present in the respective Distillates

fourth of that present in Arab Heavy and less than one-half of that present in Arab Medium. This also indicates that more basic species such as pyridines, amides and other basic compounds are present in Arab Heavy and Arab Medium distillates. The calculated empirical formulae and the vapor pressure osmometric determined average molecular weights suggested that the mass of an average molecule decreases from Arab Heavy to Arab Berri through Arab Medium and Arab Light distillates. The data also suggest that Arab Heavy and Arab Medium distillates contain molecules of higher mass than Arab Light and Arab Berri distillates. The data obtained from these three methods suggest that Arab Heavy and Arab Medium distillates may have more nitrogen compounds than the other two distillates. Therefore, the Arab Heavy and Arab Medium distillates were selected for further characterization.

5.6 DISTRIBUTION OF CLASSES OF COMPOUNDS IN THE HIGH-BOILING PETROLEUM DISTILLATES(370-535°C)

The nitrogen content of Arab crude distillates are very low and the number of nitrogen compounds expected is very large and thus the concentration of any nitrogen compound type in these distillates is expected to be very less. Therefore, the separation and concentration procedures of nitrogen compounds from these distillates are of prime importance. The separation scheme (1) designed by USBM-API project was used to separate the high-boiling distillates (370-535°C) from Arab Heavy and Arab Medium crude oils into four major classes of compounds namely acids, bases, neutral nitrogen compounds and hydrocarbons. The acids, bases and neutral nitrogen compounds collectively are called

polar compounds or polar concentrate. Table 21 shows the yields of these fractions in the two distillates. In each distillate, the weight percent of neutral nitrogen compounds are higher than the bases which in turn are higher than the acids. The total weight percent of acids, bases and neutral nitrogen compounds are higher in Arab Heavy as compared to Arab Medium distillate.

The terms acid, base and neutral nitrogen compound have operational significance rather than chemical. Acids are defined as compounds which are separated from petroleum and related materials by the use of anion-exchange resin. The resins used for these purposes may be different for different types of material but they are normally strong anion resins. The acid fraction generally contains compounds identified as phenols and carboxylic acids. It also includes amides and pyrrolic compounds which are not organic acids normally. The pyrroles and amides are separated as acids probably because they form hydrogen bonds with anion resin (39).

Similarly, bases are defined as compounds which are separated from the oil using a strong cation-exchange resin. The base fraction consists of nitrogen compounds such as pyridines and amides. The pyridines are titrated as strong bases while amides as weak bases. The base fraction may also contain nitrogen compounds which are nontitratable such as pyrroles. The pyrrolic compounds such as carbazoles are removed in the base fraction due to perhaps they form hydrogen bonds with the cation resin (39).

The neutral nitrogen compounds are defined as compounds separated

TABLE 21

YIELD OF ACIDS, BASES AND NEUTRAL NITROGEN COMPOUNDS SEPARATED FROM DISTILLATES(370-535^{O}C)

	WEIGHT PERCENT OF DISTILLATE				
DISTILLATE	ACIDS	BASES	NEUTRAL NITROGEN COMPOUNDS	HYDROCARBONS	RECOVERY
ARAB HEAVY	1.85	1.93	2.05	94.47	100.30
ARAB MEDIUM	1.56	1.72	2.00	94.92	100.20

from the oil by complexation with ferric chloride-attapulgus clay. The neutral nitrogen fraction normally contains certain pyrrolic compounds and amides which are not retained either by anion or cation-exchange resins. These compounds coordinate with ferric chloride to form a coordination complex (39).

5.7 CHARACTERIZATION OF ACIDS, BASES AND NEUTRAL NITROGEN COMPOUNDS

The acids, bases and neutral nitrogen compounds obtained from Arab Heavy and Arab Medium distillates were characterized by infrared spectroscopy. The infrared spectra of these fractions were found to contain similar compound types. Figure 11 shows the infrared spectra of acids, bases and neutral nitrogen fractions separated from Arab Heavy distillate. The infrared spectrum of base fraction (AHB) shows bands at 1598 cm^{-1} and 1567 cm^{-1} which are characteristics of pyridine compound types. The spectrum also shows a band at 1640 cm^{-1} with shoulder at 1690 cm^{-1}. The acid (AHA) and neutral nitrogen fractions (AHN) also show these bands but they are less strong and prominent as compared to base fraction. These bands are characteristics of five and six membered cyclic amides. Infrared spectrum of acid fraction (AHA) exhibits a broad strong band at 3350 cm^{-1} while in neutral fraction it is at 3400 cm^{-1}. This band is almost absent in base fraction spectrum. This band around 3400 cm^{-1} may be due to the intermolecularly bonded hydroxyl functional groups present. A similar trend is observed among infrared spectra of acids, bases and neutral nitrogen fractions obtained from Arab Medium distillate which are shown in Figure 12. The base fraction (AMB) exhibits a broad and strong band at 1580 cm^{-1}. This

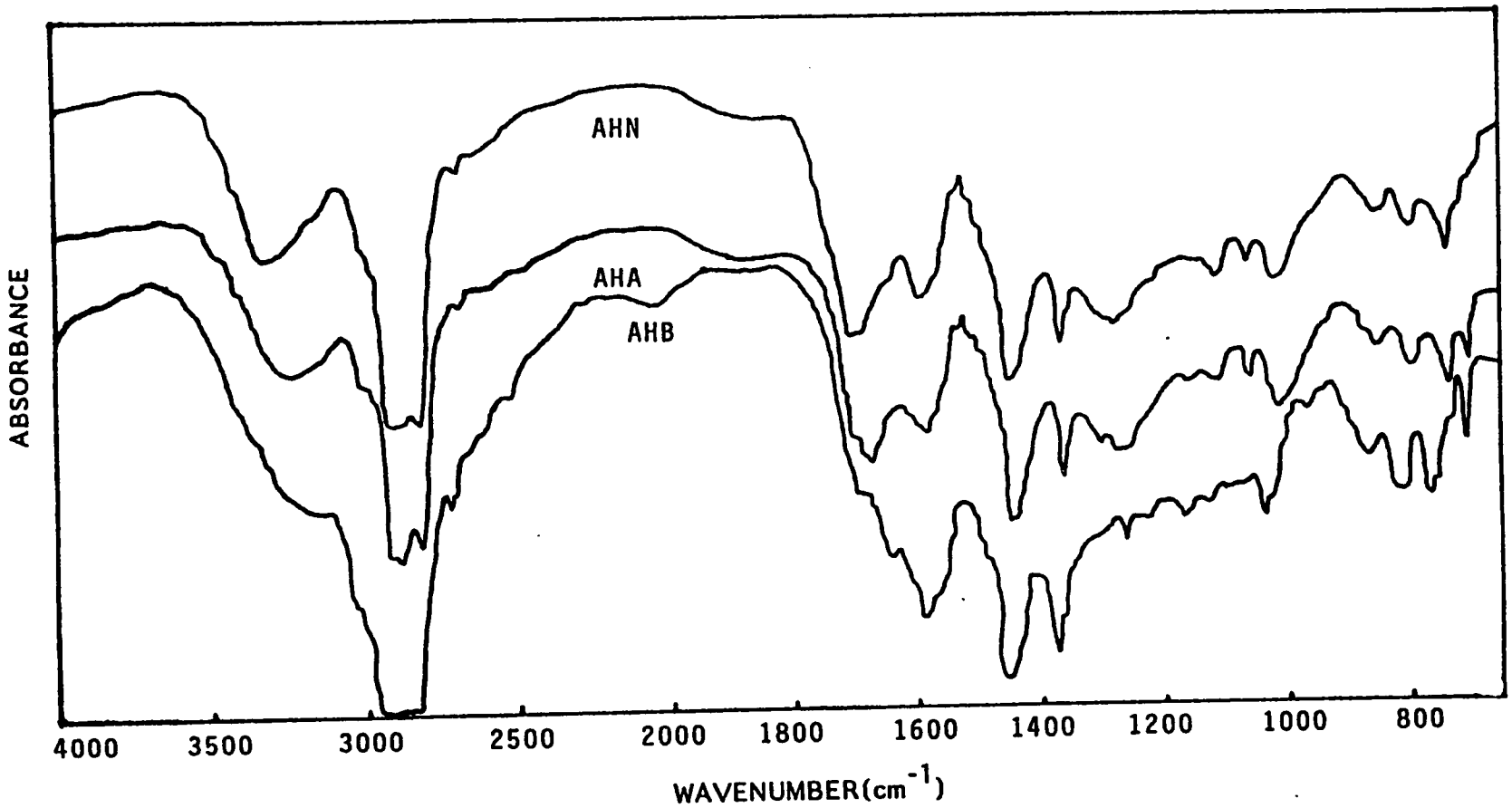


Figure 11. Infrared Spectra of Acids(AHA), Bases(AHB) and Neutral Nitrogen Compounds(AHN) Separated from Arab Heavy High-Boiling Distillate (370-535°C)

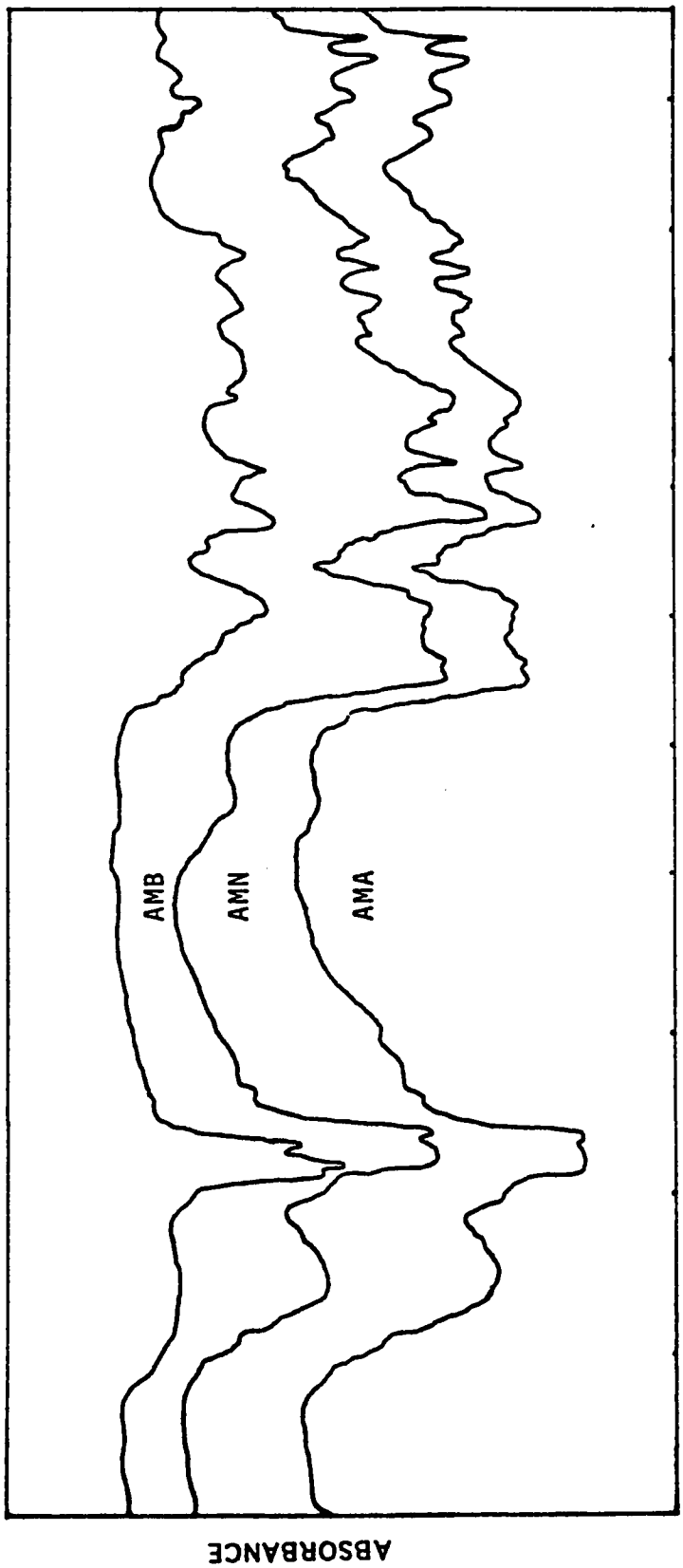


Figure 12. Infrared Spectra of Acids(AMA), Bases(AMB) and Neutral Nitrogen Compounds(AMN) Separated from Arab Medium High-Boiling Distillate (370-535°C)

band is also present in the spectra of acid and neutral fractions. This band is an indication of presence of pyridine type compounds. The acid (AMA) and neutral nitrogen fractions (AMN) show similar broad absorption band at around 1700 cm^{-1} which is absent in base fraction. This band appears due to the presence of carboxylic acids. The acid and neutral fractions show identical absorption band at around 3200 cm^{-1}. This band is absent in base fraction. So on the whole it is infered that the acid fraction contains amide and pyrrole type nitrogen compounds along with phenols and carboxylic acids. The infrared spectrum of basic fraction shows the presence of pyridines, amides and pyrrolic functionalities. Similarly, the infrared spectrum of neutral nitrogen fraction suggest that amide and pyrrole type nitrogen compounds are present in this fraction. Because of the overlapping of the similar nitrogen compound types in the acids, bases and neutral nitrogen fractions, it was decided to combine the three fractions into one "total polar concentrate" for both Arab Heavy and Arab Medium distillates separately. Each of the total polar concentrate was then separated into smaller fractions by HPLC, and these fractions were analyzed by infrared spectroscopy, potentiometric titration and gas chromatography-mass spectrometry.

5.8 SEPARATION OF POLAR CONCENTRATE INTO NITROGEN COMPOUND TYPES BY ADSORPTION CHROMATOGRAPHY

The acids, bases and neutral nitrogen fractions from Arab Heavy and Arab Medium distillates were combined separately to give total polar concentrates. The polar concentrate represented 5.83 and 5.18 weight percent of the Arab Heavy and Arab Medium distillates respectively.

For both distillates, the polar concentrate was dissolved in benzene to give a benzene soluble and a benzene insoluble fraction. The benzene soluble material was used for further characterization and identification work. The benzene insoluble material was gummy in appearance and looked like resins. The yield of the benzene soluble (nitrogen concentrate) and benzene insoluble (resins) in terms of weight percent of distillate is given in Table 22. The weight percent of nitrogen concentrate is higher for Arab Heavy(4.87) as compared to Arab Medium(4.41).

The resins represented 16.46 and 14.86 weight percent of the respective Arab Heavy and Arab Medium polar concentrate. This material could not be defined by infrared spectroscopy and produced no identifiable peaks in the gas chromatographic analysis using nitrogen phosphorus detector (NPD) even at its highest sensitivity. These resins were subjected to total mass spectral analysis. The total mass spectra of Arab Heavy and Arab Medium resins are shown in Figures 13 and 14. These spectra show more intense and abundance of peaks below 60 m/e. The higher m/e peaks are of low intensity and few. Both spectra show peaks at even and odd m/e values belonging to different m/e series responsible for different classes of compounds. The mass spectra of Arab Medium resin have peaks at higher m/e values in these series and more intense as compared to mass spectra of Arab Heavy resin. Both of the Arab Heavy and Arab Medium resins have a series of ions at 28,42,56,70,84,.....etc. m/e number. This series is characteristic of alkenes and cycloalkanes having general formula $C_nH_{2n}^+$ (131). The series of ions present at m/e values

TABLE 22

YIELD OF NITROGEN CONCENTRATE AND RESIN MATERIAL SEPARATED FROM POLAR CONCENTRATE

	WEIGHT PERCENT OF DISTILLATE		
DISTILLATE	POLAR CONCENTRATE	NITROGEN CONCENTRATE	RESIN
ARAB HEAVY	5.83	4.87	0.96
ARAB MEDIUM	5.18	4.41	0.77

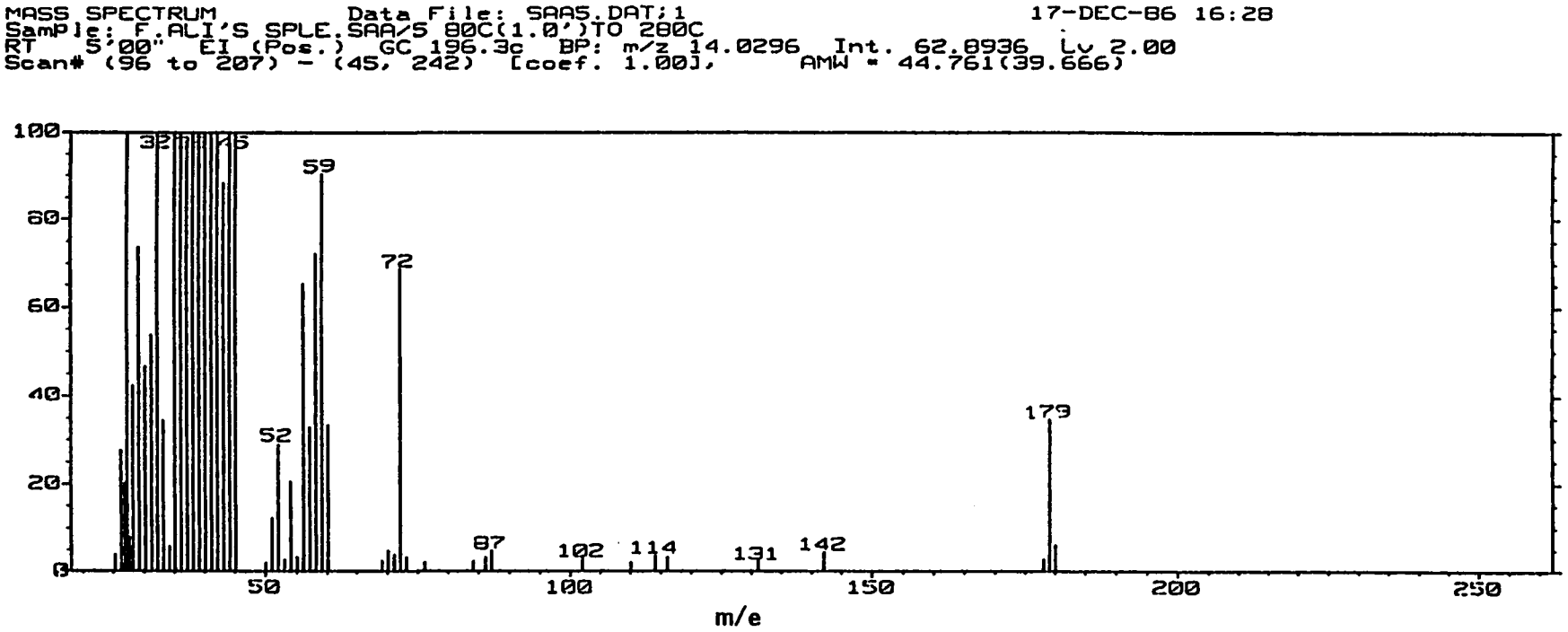


Figure 13. Total Mass Spectrum of Arab Heavy Resin Material

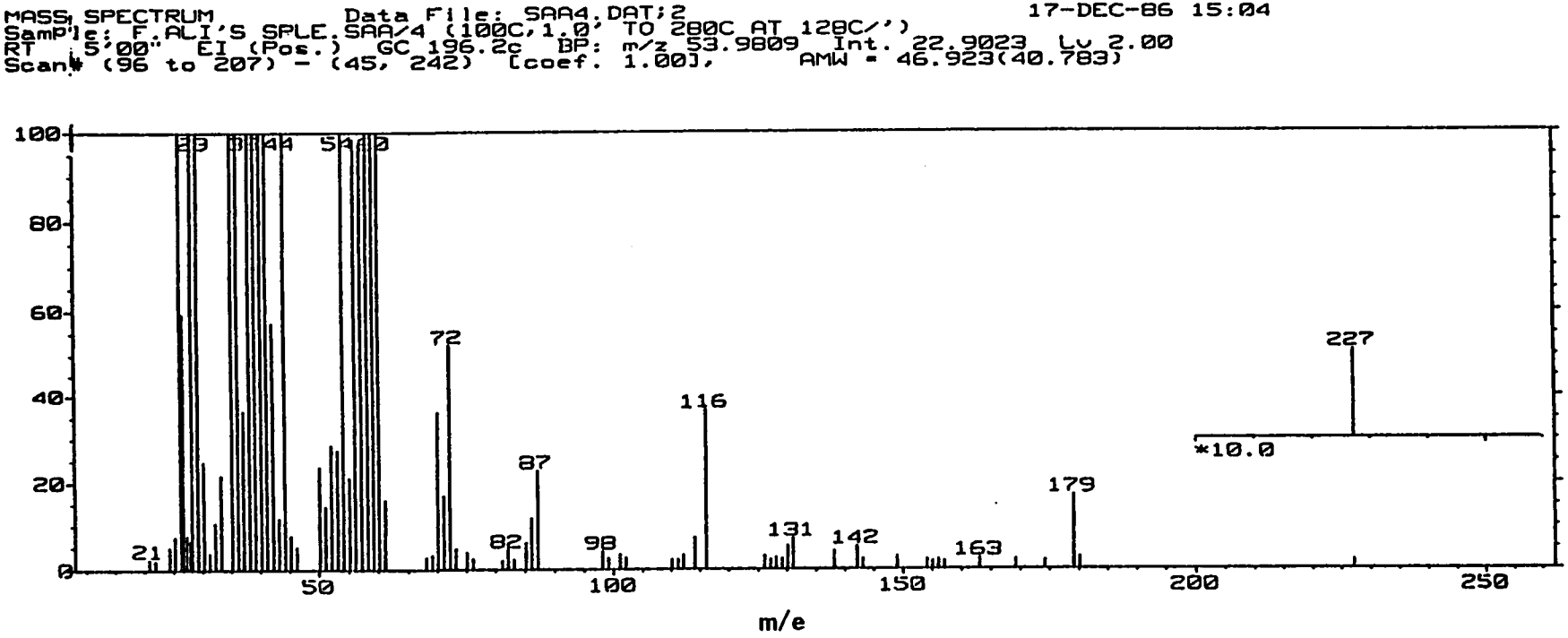


Figure 14. Total Mass Spectrum of Arab Medium Resin Material

29,43,57,71,85,.....etc. is characteristic of aldehydes and ketones having general formula $C_nH_{2n-1}O^+$. Both spectra also contain ions at 30,44,58,72,86,.....etc. m/e values which are characteristic of amines represented by the formula $C_nH_{2n+2}N^+$. There is a series of ions at 45,59,73,87,.....etc. m/e values which represents acids and esters having general formula $C_nH_{2n-1}O^+$. This series of ions also represent saturated alcohols and ethers having formula $C_nH_{2n+1}O^+$. In addition, the spectra of Arab Medium resin have a series of ions at 40,54,68,82,.....etc. m/e values and thought to arise from nitrile compounds of the general formula $C_nH_{2n-2}N^+$ (131). Both spectra show peak at 179 which could not be identified. A mixture of six nitrogen compounds was also subjected to mass spectral analysis at similar conditions to get various fragments containing nitrogen. The mass spectrum for this mixture is shown in Figure 15. Holmes and Latham (86) in their study of nitrogen compound types in Paraho shale oil have reported similar benzene insoluble resinous matter and suggested that the formation of this matter could be due to a possible contamination of the concentrate from the ion-exchange resins and/or the clay. The recovery percentage as shown in Table 21 for Arab Heavy and Arab Medium distillates do not, however, show a significant increase as would be expected in case of contamination. Due to the insolubility of this material and subsequent problems in further fractionation, the resins (benzene insolubles) were not studied any further. Thus, only nitrogen concentrates (benzene solubles) were subjected to further nitrogen compound types fractionation and characterization.

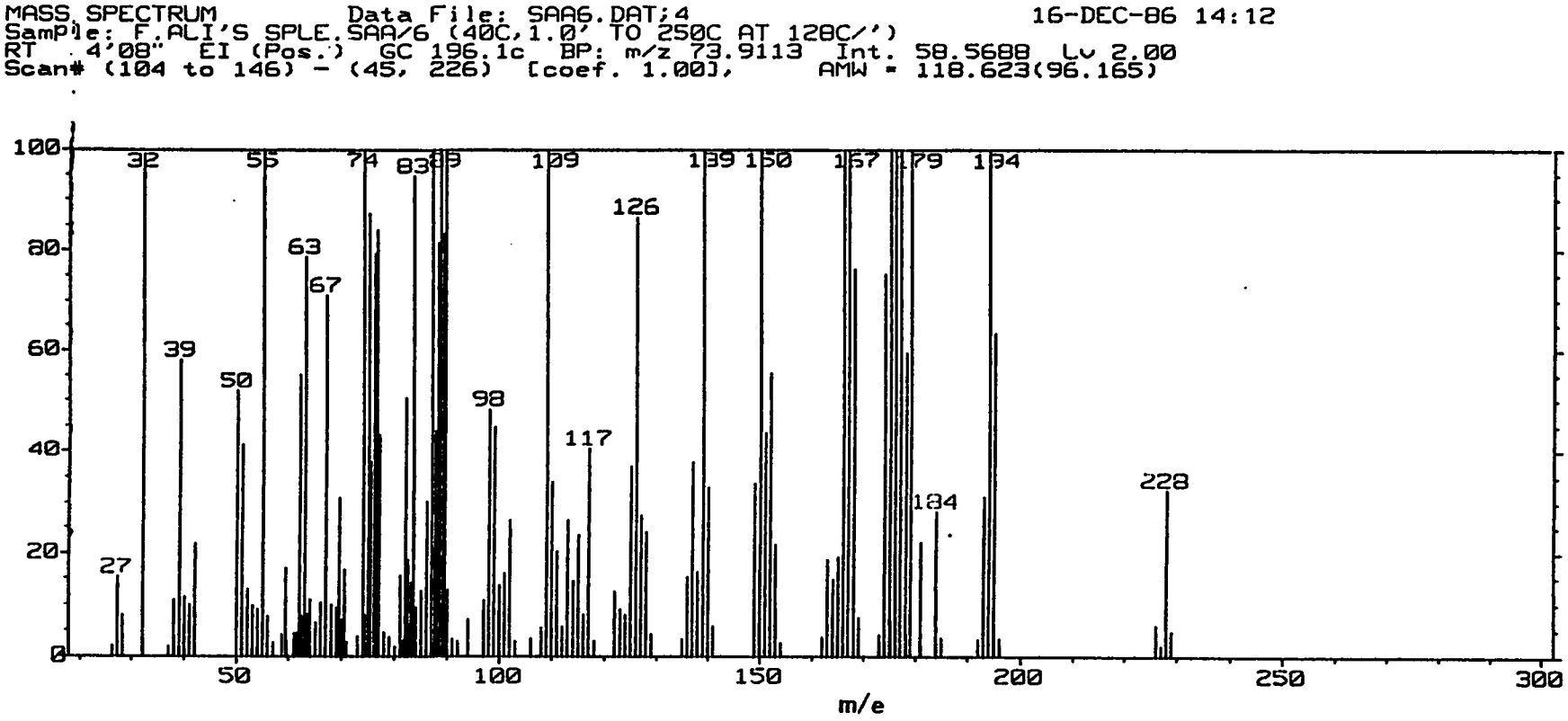


Figure 15. Total Mass Spectrum of Synthetic Mixture of Six Compounds. The Compounds are Indole(117), Carbazole(167), Anthracene(178), Acridine(179), Phenanthridine(179) and Caffeine(194).

The Arab Heavy and Arab Medium nitrogen concentrates were individually chromatographed by HPLC on neutral alumina to separate the material into three distinct nitrogen compound types. Table 23 shows the amount of these three fractions in terms of weight percent of nitrogen concentrate obtained from HPLC of Arab Heavy and Arab Medium nitrogen concentrates. The weight percent of fraction I is higher than fraction II which in turn is higher than fraction III in both distillates. The weight percent of fraction I and III is higher and that of fraction II is lower for Arab Heavy as compared to Arab Medium distillate. The percent recovery of the material in the HPLC fractionation step of nitrogen concentrate was almost 100 percent. The three fractions obtained from HPLC of Arab Heavy nitrogen concentrate were designated as AHF-I, AHF-II and AHF-III while those of Arab Medium as AMF-I, AMF-II and AMF-III. The fraction AHF-I and AMF-I fractions were obtained by elution with 5-50 percent solution of 1,2-dichloroethane in cyclohexane, the fractions AHF-II and AMF-II with 50-100 percent solution of 1,2-dichloroethane in cyclohexane and the fractions AHF-III and AMF-III with 40 percent methanolic solution of benzene (86).

5.9 CHARACTERIZATION OF HPLC FRACTIONS

The HPLC fractions separated from the fractionation of nitrogen concentrate from Arab Heavy and Arab Medium distillates were analyzed by infrared spectroscopy, ultraviolet spectroscopy, potentiometric titration, gas chromatography and gas chromatography-mass spectrometry. The results of these techniques are discussed in the following sections.

TABLE 23

YIELD OF FRACTIONS OBTAINED FROM HPLC OF NITROGEN CONCENTRATE ON NEUTRAL ALUMINA

NITROGEN CONCENTRATE	HPLC FRACTIONS WEIGHT PERCENT OF NITROGEN CONCENTRATE		
	FRACTION-I	FRACTION-II	FRACTION-III
ARAB HEAVY	45.13	32.46	22.41
ARAB MEDIUM	43.78	34.90	21.32
	WEIGHT PERCENT NITROGEN IN FRACTION		
ARAB HEAVY	3.24	3.08	2.97
ARAB MEDIUM	3.11	2.93	2.85

5.9.1 INFRARED SPECTROSCOPY

5.9.1.1 QUALITATIVE INFRARED ANALYSIS OF HPLC FRACTIONS

FRACTION-I(AHF-I and AMF-I)

These fractions were obtained from HPLC of Arab Heavy and Arab Medium nitrogen concentrates using 5-50 volume percent solution of 1,2-dichloroethane in cyclohexane. The infrared spectra of fraction-I from Arab Heavy(AHF-I) and Arab Medium(AMF-I) distillates are compared in Figure 16. Both fractions show similar infrared spectra. The spectrum of AMF-I is well resolved in the far infrared region showing sharp absorption bands. Both spectra show prominent C=N stretching vibrations at 1590 cm^{-1} and 1570 cm^{-1}. These absorption bands are characteristics of pyridine derivatives like benzoquinolines and dibenzoquinolines (132). The IR spectrum of AHF-I exhibited a weak band at 3600 cm^{-1} characteristics of phenolic compounds. This band is the result of O-H stretching vibration of phenols. This band is accompanied by a broad weak band around 3350 cm^{-1} which may be due to the intermolecularly bonded hydroxyl functional groups. The absorption band at 3600 cm^{-1} is not present in AMF-I spectrum. Also the band at 3350 cm^{-1} is relatively weak. Both fractions show a moderate absorption band around 1715 cm^{-1} and a very weak band around 3200 cm^{-1}. These bands are characteristics of carboxylic acids like naphthenic acids and higher benzologs. The band at 1715 cm^{-1} may be assigned to carbonyl(C=O) stretching vibration while the band at 3200 cm^{-1} may be due to the stretching vibration of hydrogen bonded hydroxyl groups of carboxylic acids. The IR spectrum of AMF-

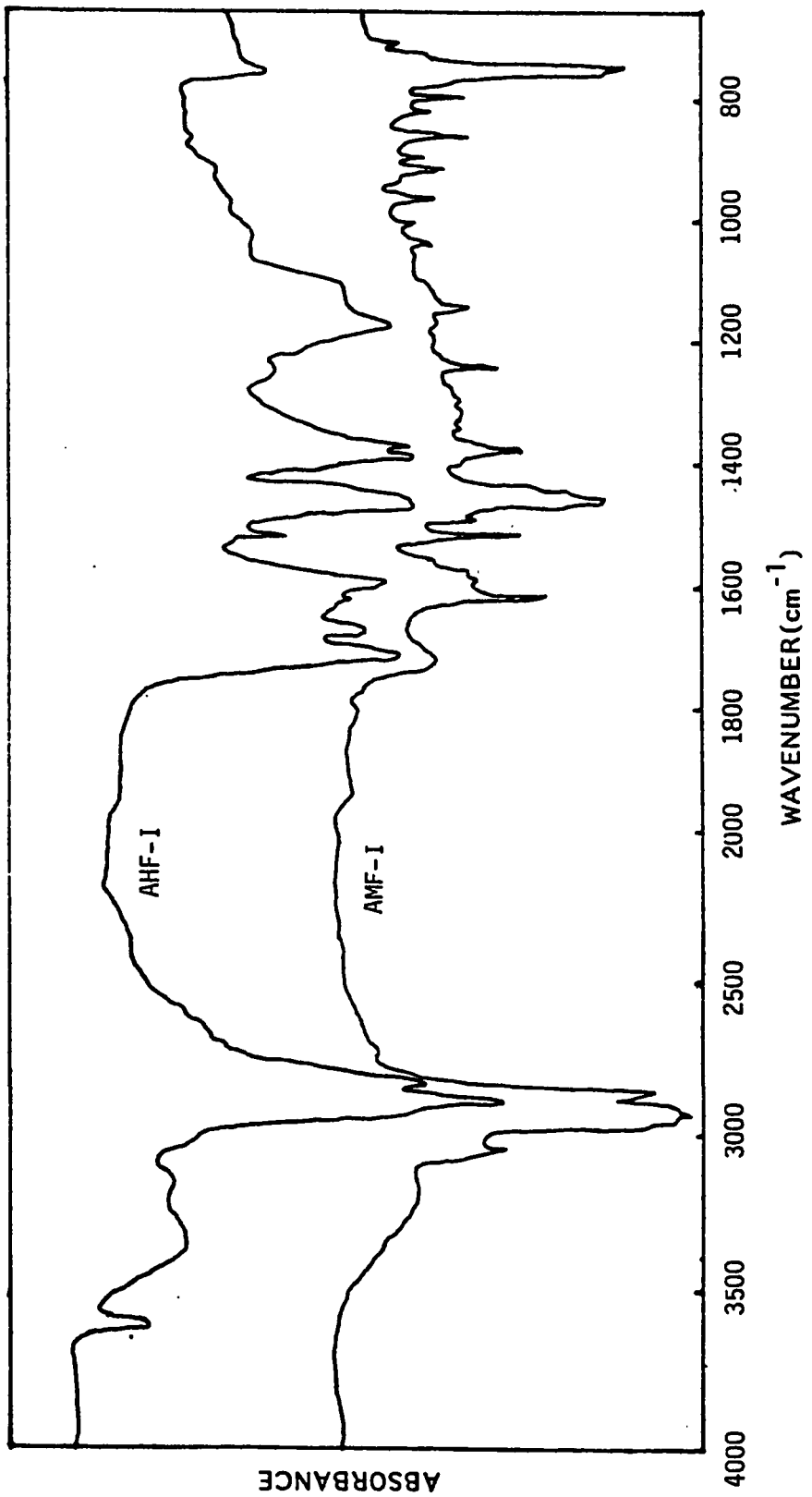


Figure 16. Infrared Spectra of AHF-I and AMF-I Fractions

I has no absorption around 1670 cm^{-1} but AHF-I spectrum shows a weak band in this region which is characteristic of six membered ring amide compounds. The N-H stretching vibration at 3350 cm^{-1} of amides is probably overlapped by broad O-H absorption. These amides may also be N-substituted. The IR spectra of both AMF-I and AHF-I show weak absorption bands around 3100 cm^{-1} which are due to stretching vibration of C-H aromatic groups.

Both fractions show strong absorption bands arising from paraffinic C-H absorption in the region 2830-3000 cm^{-1}. These bands are intense and arise from C-H asymmetrical and symmetrical stretching vibration. This shows that in these fractions, there are large number of methylene and methyl linkages.

The appearance of weak combination and overtone bands in the region 1800-2000 cm^{-1} are also observed in both fractions. The pattern of the overtone bands is characteristic of the substitution pattern of the ring in aromatic and heterocyclic compounds

On the basis of Infrared analysis, it can be said that the fraction-I from both Arab Heavy and Arab Medium crudes may consists mostly of pyridines benzologs along with traces of carboxylic acids and phenols. The fraction-I from Arab Heavy may also contain traces of amide type compounds.

FRACTION-II(AHF-II and AMF-II)

These fractions were obtained from HPLC of Arab Heavy and Arab Medium nitrogen concentrate using 50-100 volume percent solution of

1,2-dichloroethane in cyclohexane. The infrared spectra of fraction-II from Arab Heavy(AHF-II) and Arab Medium(AMF-II) are compared in Figure 17. Both the spectra exhibited similar infrared absorption bands. Both spectra show strong and predominant bands at 3450 cm^{-1} which is characteristic of pyrrole derivatives like carbazoles and benzcarbazoles (132). These bands arise from N-H stretching vibration of these compounds. Pyrrolic compounds are also confirmed by the absorption band at 1330 cm^{-1} in both spectra which is thought to arise from C-N stretching vibration. Also, weak C=N stretching band at 1585 cm^{-1} indicating pyridine benzologs and weak C=O stretching vibration indicating amides are observed in the spectrum of AHF-II fraction. The amide band is absent in AMF-II showing that amides are either absent or present in trace amount. Both spectra show very weak absorption band around 1715 cm^{-1} which is due to the presence of carboxylic acids. Both the spectra exhibited a weak band at around 3600 cm^{-1} due to the O-H stretching vibration of phenols. The broad band at 3220 cm^{-1} in AHF-II may be due to intermolecularly bonded hydroxyl functional groups. Overtones or combination bands are observed in both fractions in the region 2000-1800 cm^{-1} which show substitution pattern in aromatic compounds. The IR spectra of both fractions show C-H absorption bands due to the aliphatic as well as aromatic systems. Presence of phenols is also established by absorption bands at 1240 cm^{-1} due to the C-O stretching vibration. On the whole, it can be infered that the fraction II from Arab Heavy and Arab Medium consist mostly of pyrroles derivatives along with traces of pyridines, phenols and amides.

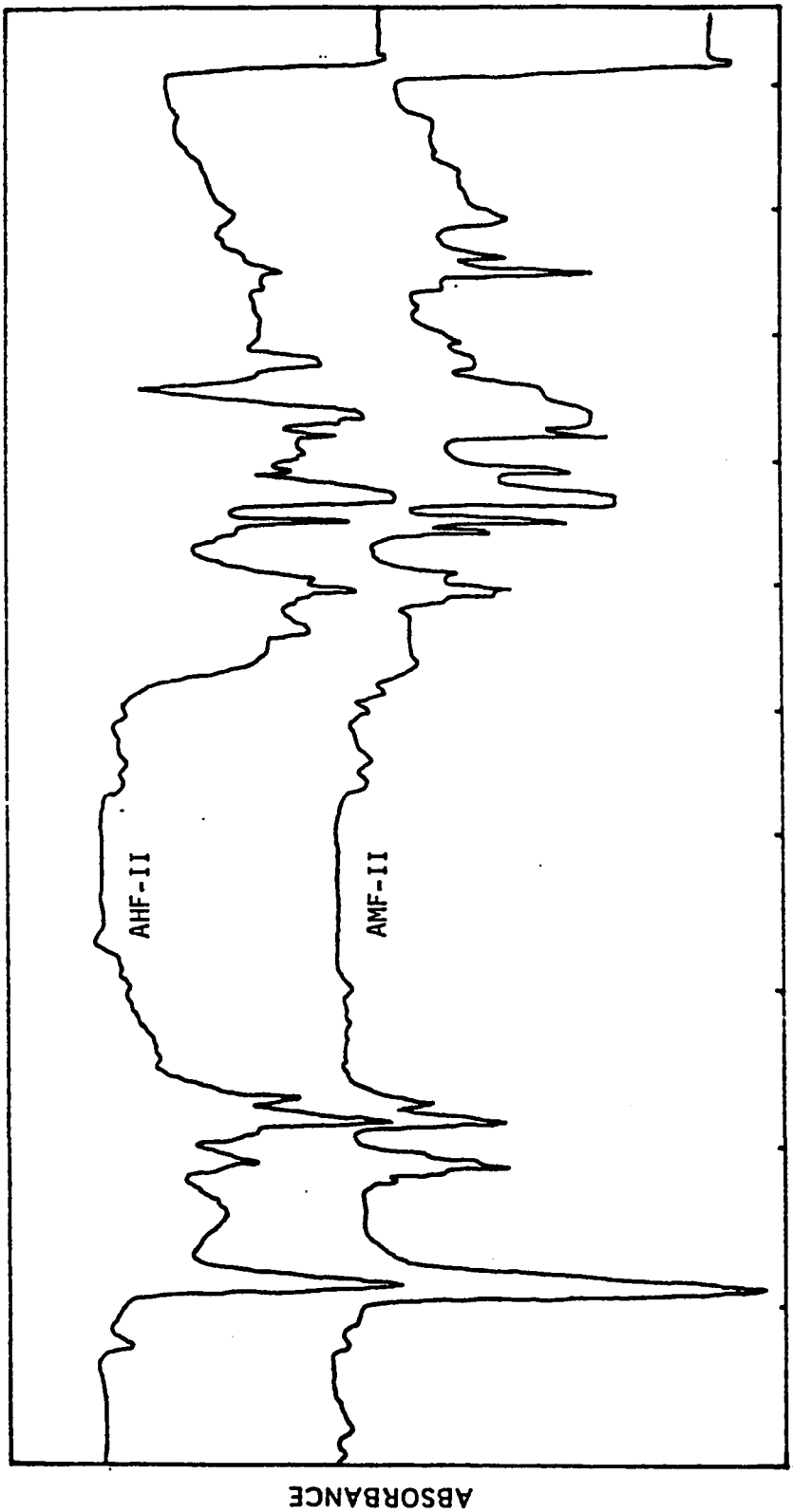


Figure 17. Infrared Spectra of AHF-II and AMF-II Fractions

FRACTION-III(AHF-III and AMF-III)

These fractions were obtained from HPLC of Arab Heavy and Arab Medium nitrogen concentrate using 40 volume percent solution of methanol in benzene. The infrared spectra of fraction-III both from Arab Heavy(AHF-III) and Arab Medium(AMF-III) are compared in Figure 18. Both spectra exhibited almost similar pattern with little difference in peak intensities or frequencies. Both fraction show a strong band at 1675 cm^{-1} with shoulder at 1682 cm^{-1} which are characteristics of six membered amides like pyridones and higher benzologs. These bands arise from carbonyl(C=O) stretching vibrations. Both fraction also show a sharp band at 3400 cm^{-1} due to the N-H stretching vibration of amide compounds. The presence of amides is also confirmed by the strong band at 1365 cm^{-1} which is thought to be due to C-N stretching vibration (132). The absorption band at 3620 cm^{-1} is observed in IR spectra of both fractions indicating the presence of phenols due to O-H stretching vibration. Both fractions also exhibited a band at 1240 cm^{-1} due to C-O stretching vibration. Both fractions contain long aliphatic chains exhibited by C-H strong absorption bands around 2900 cm^{-1} due to the methylene and methyl groups. On the whole, it can be concluded that the AHF-III and AMF-III contain mostly amides along with some phenols.

These infrared results indicate that AHF-I and AMF-I contain mostly pyridine type nitrogen compounds, AHF-II and AMF-II contain mainly pyrrole type nitrogen compounds and AHF-III and AMF-III predominantly as amide type nitrogen compounds. The Infrared results

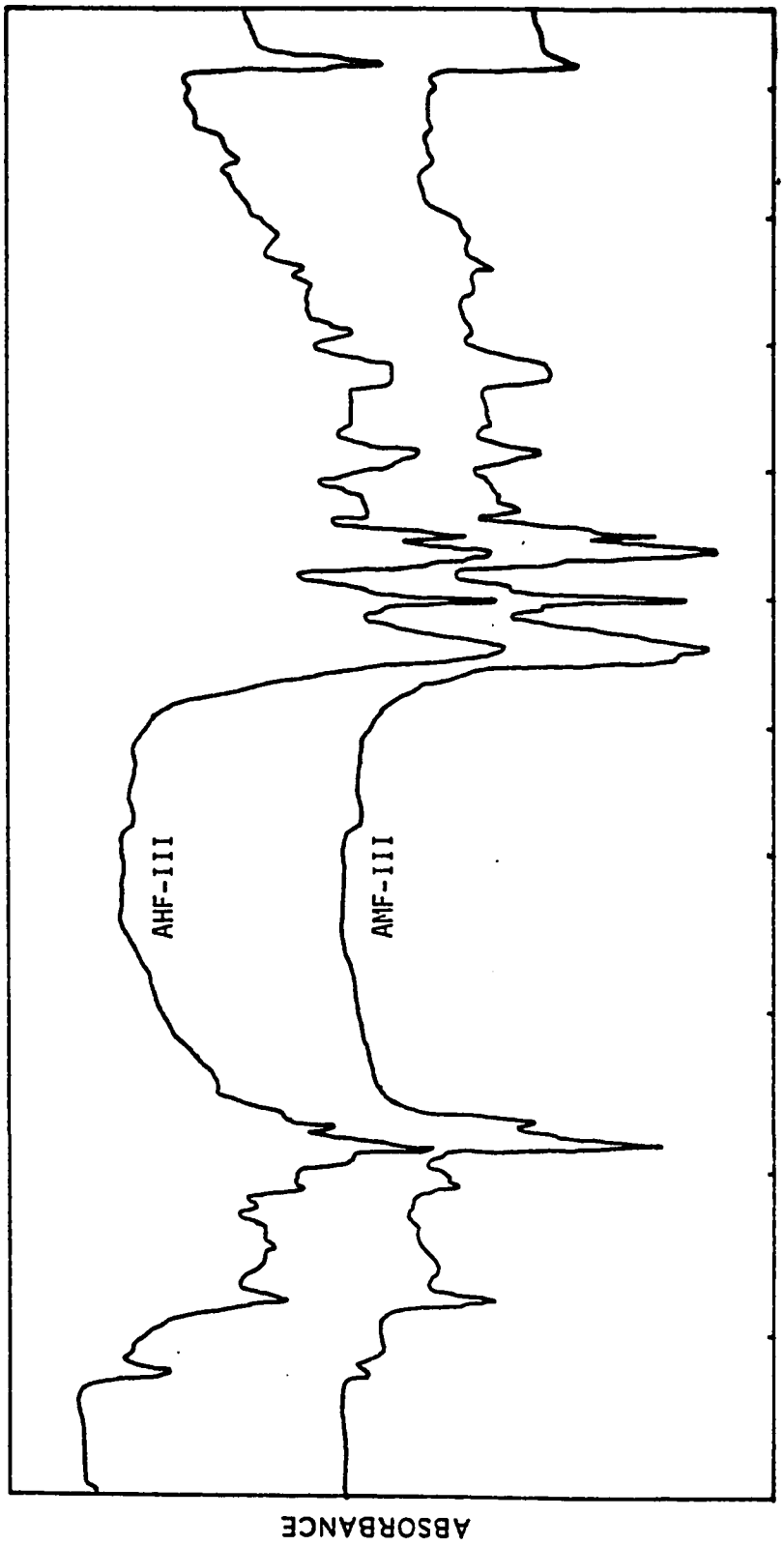


Figure 18. Infrared Spectra of AHF-III and AMF-III Fractions

further indicate that the separation of polar concentrate into pyridine, pyrrole and amide type nitrogen compounds has been achieved successfully. The characteristic frequencies observed for different type of nitrogen compounds in all three fractions are listed in Table 24. The infrared spectra of these fractions are also presented in data form in Table 25 and 26.

5.9.1.2 QUANTITATIVE INFRARED ANALYSIS OF HPLC FRACTIONS

Infrared spectroscopy was used to estimate the amount of different compound types present in HPLC fractions. Quantitative infrared spectra were recorded for six HPLC fractions as solution in spectro grade 1,2-dichloroethane. The concentration of the solutions was in the range of 15-20 mg ml^{-1}. The cells were made up of potassium bromide and the cell path length was 0.125 mm. The areas of the selected absorption bands present in each spectrum were measured in cm^{-1} by planimeter. The area of the band responsible for each compound type was divided by the integrated absorption intensity of that compound and it yielded the concentration of that compound type in moles/litre in that fraction. Integrated absorption intensities were taken from the work of McKay (40,41). These values of integrated absorption intensity are given in Table 27 for all estimated compound types. The values were converted into weight percent assuming that the molecular weight of these compound types are same. The amount of compound types calculated in terms of weight percent of each fraction are given in Table 28. The compound types found in these fractions were pyridines, pyrroles, amides, phenols and carboxylic acids. The amount of these compound types were then used to calculate the amount of strong, weak

TABLE 24

CHARACTERISTIC INFRARED FREQUENCIES OBSERVED FOR DIFFERENT TYPES OF COMPOUND IN THE SPECTRA OF HPLC FRACTIONS

FREQUENCY (cm^{-1})	ASSIGNMENT
3600	O-H Stretching (Phenols)
3460	N-H Stretching (pyrroles)
3400	N-H stretching (Amides)
3350	O-H stretching (Intermolecularly bonded Phenolic O-H)
3200	O-H stretching (carboxylic Acids) Dimers
1715	C=O Stretching (Carboxylic Acids) Dimers
1670	C=O Stretching (Amides)
1590	C=N Stretching (Pyridines)
1570	C=N Stretching (Pyridines)
1360	C-N Stretching (Pyrroles)
1350	O-H Bending (Phenols)
1240	C-O Stretching (Phenols)

TABLE 25

INFRARED SPECTRAL DATA OF HPLC FRACTIONS OBTAINED FROM ARAB HEAVY NITROGEN CONCENTRATE

AHF-I

3600(W) 3350(WB) 3150(VW) 2900(VS) 2820(S) 1715(S) 1670(W) 1620(VW) 1589(S) 1515(W) 1460(S) 1385(S) 1370(S) 1250(VW) 1170(S) 1110(W) 1025(VW) 750(W)

AHF-II

3630(VW) 3450(S) 3220(WB) 3050(W) 2970(VW) 2920(S) 2850(W) 1715(VW) 1670(W) 1610(W) 1585(W) 1500(S) 1460(S) 1420(VW) 1390(VW) 1360(W) 1330(W) 1250(W) 1100(VW) 1010(VW)

AHF-III

3610(W) 3390(S) 3210(VW) 3150(VW) 3100(W) 2910(S) 2840(W) 1665(SB) 1590(S) 1530(S) 1500(W) 1450(WB) 1360(WB) 1230(W) 1170(W) 1095(VW) 1070(VW) 1020(VW) 900(W) 750(S)

TABLE 26

INFRARED SPECTRAL DATA OF HPLC FRACTIONS OBTAINED FROM ARAB MEDIUM NITROGEN CONCENTRATE

AMF-I

3150(VW) 3050(W) 2930(VS) 2860(VS) 1715(W) 1615(S) 1585(W) 1570(W) 1550(W) 1510(S) 1490(VW) 1460(S) 1375(W) 1240(S) 1140(S) 1040(W) 995(W) 950(W) 910(W) 890(W) 860(W) 820(W) 790(W) 750(W) 745(S)

AMF-II

3630(VW) 3450(VS) 3110(VW) 3060(S) 2920(S) 2860(W) 1720(VW) 1610(W) 1575(W) 1520(S) 1500(S) 1460(SB) 1420(S) 1380(S) 1250(W) 1210(VW) 1100(S) 1075(W) 1015(W)

AMF-III

3630(VW) 3550(VWB) 3400(W) 3300(VWB) 3170(VW) 3050(W) 3020(W) 2920(S) 2840(W) 1676(VS) 1600(VS) 1525(VS) 1500(S) 1460(W) 1370(WB) 1240(WB) 1080(VW) 910(VW)

TABLE 27

INTEGRATED ABSORPTION INTENSITY VALUES OF DIFFERENT COMPOUND TYPES SELECTED FOR QUANTITATIVE INFRARED ANALYSIS

COMPOUND TYPE	FREQUENCY OF ABSORPTION cm^{-1}	INTEGRATED ABSORPTION INTENSITY $L \times mol^{-1} \times cm^{-2}$
PYRIDINES	1589	0.31×10^4
PYRROLES	3460	0.60×10^4
AMIDES	1667	1.36×10^4
PHENOLS	3600	0.50×10^4
CARBOXYLIC ACIDS	1715	1.10×10^4

TABLE 28

THE WEIGHT PERCENT OF DIFFERENT COMPOUND TYPES DETERMINED IN HPLC FRACTIONS BY QUANTITATIVE INFRARED ANALYSIS

	WEIGHT PERCENT OF FRACTION				
FRACTION	PYRIDINES	PYRROLES	AMIDES	PHENOLS	CARBOXYLIC ACIDS
ARAB HEAVY					
AHF-I	40	_	12	17	31
AHF-II	27	43	9	10	11
AHF-III	_	_	76	24	_
ARAB MEDIUM					
AMF-I	46	_	12	_	42
AMF-II	18	60	7	6	9
AMF-III	_	_	75	25	_

and nonbasic compounds present in each fraction. The strong bases include pyridines, the weak bases consist of aliphatic and aromatic amides while the pyrroles, phenols and carboxylic acids were considered as nonbasic compounds.

Strong Bases = Pyridines

Weak Bases = Amides

NonBasic = Pyrroles + Phenols + Carboxylic Acids

The amount of these compounds calculated on weight percent of individual fraction basis are given in Table 29. The AHF-I and AMF-I fractions contained the pyridine type compounds in highest amount. The pyridines were considered as strong basic compounds and they were estimated to be higher in AMF-I(46%) than in AHF-I(40%) fraction. Pyrroles compound types were not detected in these fractions because of the presence of broad bands around 3450 cm^{-1}. Amides were estimated in both AHF-I(12%) and AMF-I(12%) fractions and were considered as weak basic compounds. Significant amount of phenolic compounds were also found in AHF-I(17%) but not detected in AMF-I fraction. carboxylic acids were also found in both fractions but were higher in AMF-I(42%) than in AHF-I (31%). On the whole, the fractions AHF-I and AMF-I contain 52 and 58 weight percent basic nitrogen compounds and 48 and 42 percent nonbasic compounds which include phenols and carboxylic acids.

Pyrrolic compounds appeared to be the prominent compound types present in AHF-II and AMF-II fractions. The amount of pyrrolic type compound in AMF-II (60%) was higher than in AHF-II (43%) fraction.

TABLE 29

THE WEIGHT PERCENT OF STRONG, WEAK AND NONBASIC COMPOUNDS DETERMINED IN HPLC FRACTIONS BY QUANTITATIVE INFRARED ANALYSIS

	WEIGHT PERCENT OF FRACTION		
FRACTION	STRONG BASES	WEAK BASES	NONBASIC
ARAB HEAVY			
AHF-I	40	12	48
AHF-II	27	9	64
AHF-III	_	76	24
ARAB MEDIUM			
AMF-I	46	12	42
AMF-II	18	7	75
AMF-III	_	75	25

Pyrroles were considered as nonbasic nitrogen containing compounds. Pyridines were also present in both of these fractions. Pyridines were found higher in AHF-II (27%) than in AMF-II (18%). The amides were also determined in both AHF-II (9%) and AMF-II (7%) fractions. Both fractions contain phenols and carboxylic acids in smaller amount. On the whole, the fractions AHF-II and AMF-II individually contained 36 and 25 weight percent basic nitrogen compounds and 64 and 75 percent nonbasic compounds respectively. The total nitrogen compounds in AHF-II and AMF-II fractions were 79 and 85 weight percent of the individual fractions respectively.

The fractions AHF-III and AMF-III contained no pyridines and pyrroles compound types. These fractions contained mostly amides while the remaining material was phenols. The quantitative infrared analysis of these fraction could not be done properly because their infrared spectra were not well resolved and the bands for other compound types were overlapped, thus produced broad bands in these spectra. Amides appeared to be concentrated mainly in these fractions. The weight percent of amides in AHF-III and AMF-III were 76 and 75 while the phenols were 24 and 25 respectively.

Table 29 shows the amount of strong, weak and nonbasic compounds present in terms of weight percent of individual fraction. A comparative look at Table 29 indicates that the strong basic compounds are more in AHF-I and AMF-I than in AHF-II and AMF-II fractions. In AHF-III and AMF-III, these compounds were not detected. Instead, they were found to contain more of the weak basic compounds.

5.9.2 ULTRAVIOLET SPECTROSCOPY OF HPLC FRACTIONS

The ultraviolet spectra of fraction-I from Arab Heavy and Arab Medium distillates (AHF-I and AMF-I) along with UV spectra of pure acridine and phenanthridine are shown in Figure 19. The shape of spectra of AHF-I and AMF-I are very similar to that of acridine showing strong absorption band at 254 nm. These absorption bands are more intense and little bit shifted as compared to acridine. This may be due to the presence of substitutions in the ring (85) The absorption band around 220 nm in these samples is characteristic of that of phenanthridine. This band is also shifted and the shift is again due to the presence of substituted phenanthridines (85). Thus the ultraviolet spectra of AHF-I and AMF-I fractions indicate that these fractions mainly consist of substituted benzoquinolines/benzoisoquinolines.

The ultraviolet spectra of fraction-II from Arab Heavy and Arab Medium distillates (AHF-II and AMF-II) are compared in Figure 20 with the UV spectrum of pure carbazole. The absorption wavelengths and the patterns are quite similar to that of the carbazole. This similarity gives evidence of the predominance of carbazoles in these fractions. The absorption bands at 259 and 283 nm are more pronounced in these fractions. This may be due to the presence of higher benzologs in these fractions such as benzcarbazoles. The shifting of the wavelength of absorption bands may be due to substitution in the carbazoles ring (85).

The ultraviolet spectra of fraction-III from Arab Heavy and Arab Medium distillates (AMF-III and AHF-III) are shown in Figure 21. A

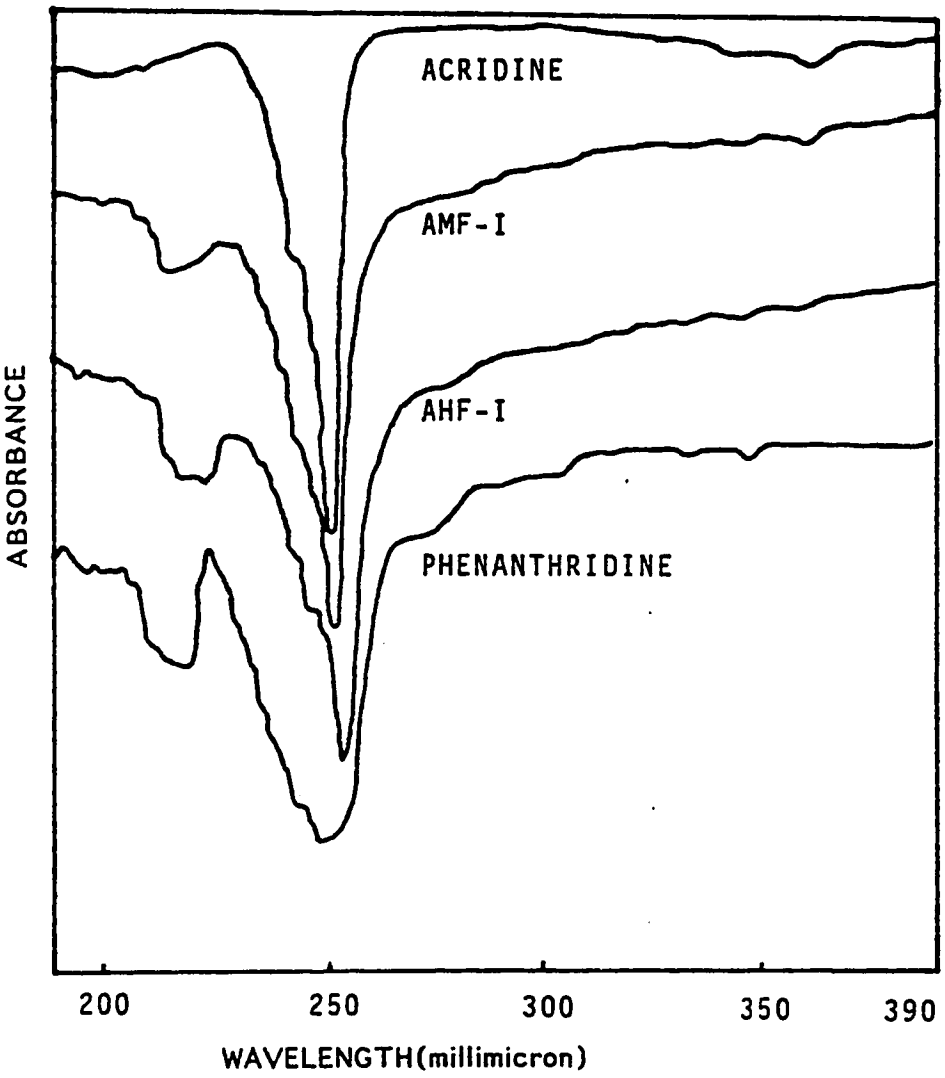


Figure 19. Ultraviolet Spectra of AHF-I and AMF-I Fractions Compared with UV Spectra of Pure Phenanthridine and Acridine

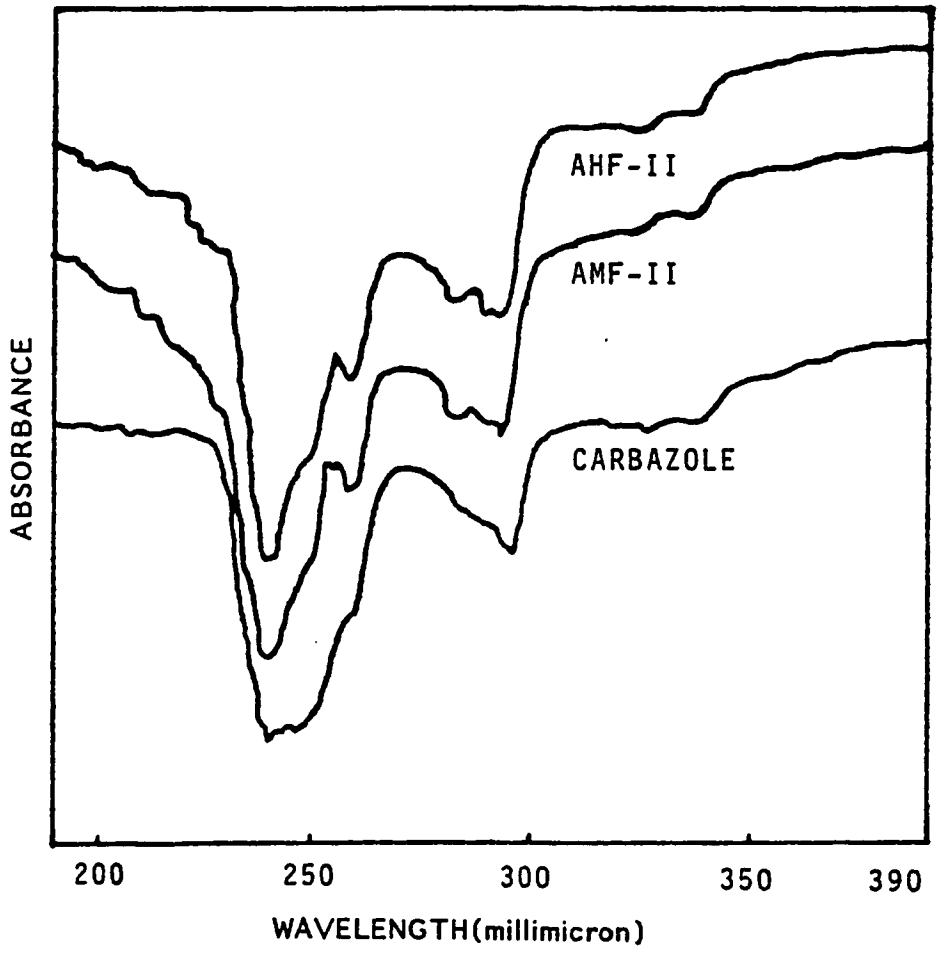


Figure 20. Ultraviolet Spectra of AHF-II and AMF-II Fractions Compared with UV Spectrum of Pure Carbazole

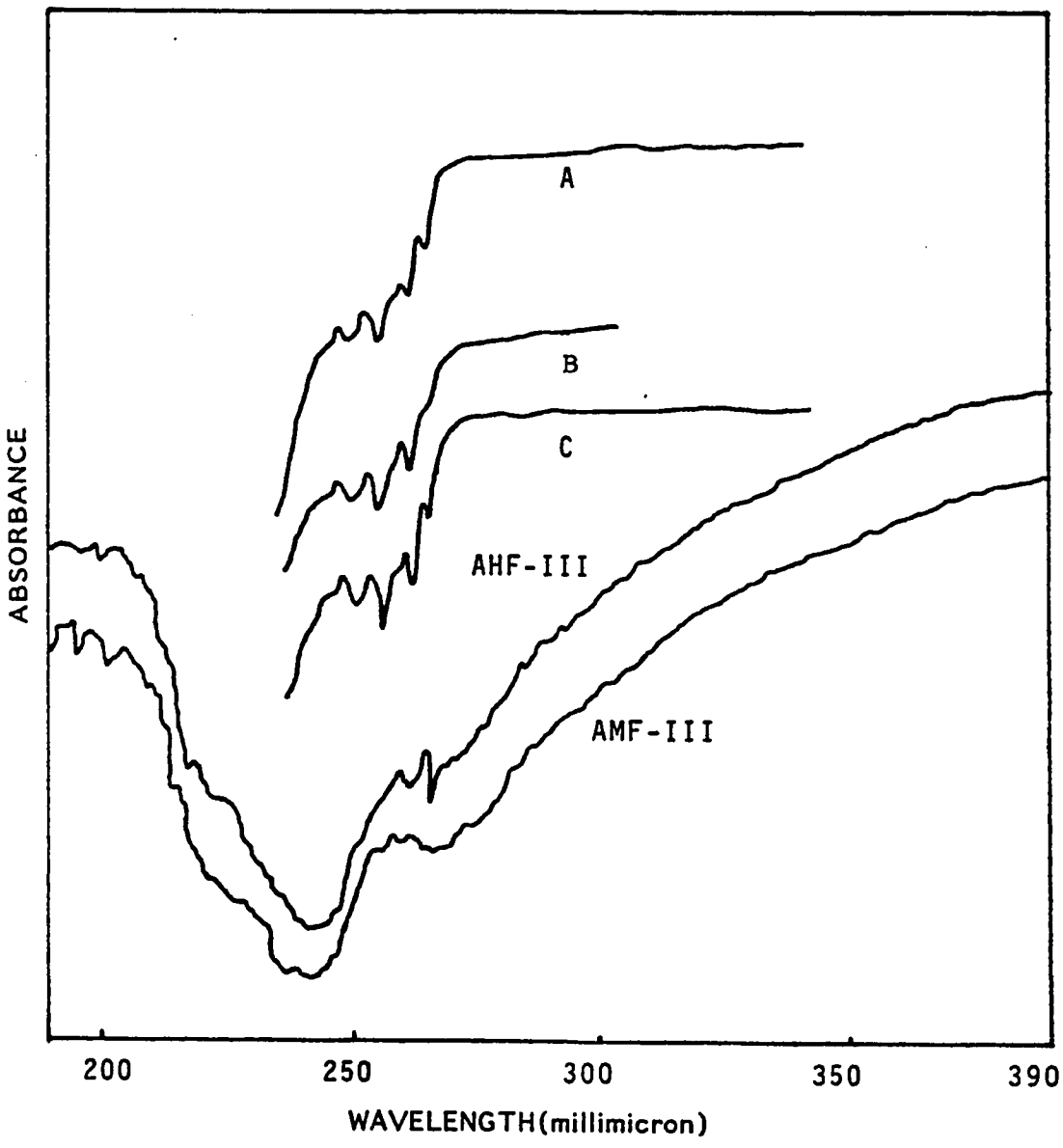


Figure 21. Ultraviolet Spectra of AHF-III and AMF-III Fractions Compared with Ultraviolet Spectra of Cyclic Amides.

A = 3-Benzyl-6-methylhydrouracil

B = 6-Phenylhydrouracil

C = 3-Benzyl-6-phenylhydrouracil

study of the available ultraviolet spectra from Sadtler Research Laboratories, Inc. (133) indicated that the cyclic amides show characteristic UV absorption in the region 240-270 nm having sharp UV bands at 246, 251, 257, 263 and 267 nm. These spectra are also plotted in Figure 21. Both AHF-III and AMF-III fractions show absorption bands in this region. The bands in these fractions are not so sharp as in the spectra of pure amides. This may be due to the fact that these fractions are a mixture of amides, phenols and other compounds as indicated already by the quantitative infrared study of these fractions. This similarity of absorption bands in the spectra of amides and these fractions indicates the possible presence of cyclic amides in AHF-III and AMF-III fractions.

5.9.3 NONAQUEOUS POTENTIOMETRIC TITRATION OF HPLC FRACTIONS

The fractions obtained from HPLC of nitrogen concentrate were titrated potentiometrically in a mixture of acetic anhydride and benzene in the volume ratio of 2:1 using perchloric acid in dioxane as titrant. Each fraction shows two inflections in the titration curve, the first for the titration of strong basic nitrogen compounds present in it while the second for the weak basic nitrogen compounds titrated. The results are given in Table 30 which shows the distribution of strong, weak and nonbasic nitrogen present in six HPLC fractions. The results are reported as weight percent of individual fractions. The amount of strong and weak basic nitrogen was calculated using the slope of Figure 8. This Table also contains total nitrogen present in each fraction which was determined by elemental analysis of these fractions. Nonbasic

TABLE 30

THE WEIGHT PERCENT OF STRONG, WEAK AND NONBASIC NITROGEN DETERMINED IN HPLC FRACTIONS BY NONAQUEOUS POTENTIOMETRIC TITRATION

FRACTION	WEIGHT PERCENT OF FRACTIONS					WEIGHT PERCENT OF TOTAL NITROGEN			
	TOTAL NITROGEN	TOTAL BASIC	STRONG BASIC	WEAK BASIC	NONBASIC NITROGEN	TOTAL BASIC	STRONG BASIC	WEAK BASIC	NONBASIC NITROGEN
ARAB HEAVY									
AHF-I	3.24	1.66	1.17	0.49	1.58	50.9	35.9	15.0	49.1
AHF-II	3.08	1.04	0.72	0.32	2.04	33.8	23.5	10.3	66.2
AHF-III	2.97	1.81	0.32	1.49	1.16	60.8	10.6	50.2	39.2
ARAB MEDIUM									
AMF-I	3.11	1.32	1.01	0.31	1.79	42.5	32.5	10.0	57.5
AMF-II	2.93	0.69	0.46	0.23	2.24	23.7	15.8	7.9	76.3
AMF-III	2.85	1.47	0.25	1.22	1.38	51.4	8.7	42.7	48.6

nitrogen was determined by the difference of total nitrogen and the total basic nitrogen present in each fraction. These values were converted into weight percent of the total nitrogen and are also reported in Table 30. This technique enabled the quantification of strong basic, weak basic and nonbasic nitrogen present in each fraction. The data in Table 30 shows that all fractions contain strong bases. The strong bases in AHF-I and AMF-I accounts for 32-36 weight percent of the total nitrogen, whereas nonbasic nitrogen containing compounds in these fractions are almost 50 percent of total nitrogen. In AHF-II and AMF-II, the majority of nitrogen containing compounds are nonbasic. These fractions contain 16-23 weight percent of strong basic nitrogen. In AHF-III and AMF-III, the weak basic nitrogen containing compounds constitute about 43-50 weight percent of the materials. The Arab Heavy possesses more basic nitrogen compounds as compared to Arab Medium. The total nitrogen is higher in Arab Heavy as compared to Arab Medium. Among the three fractions from each distillate, certain trends have been observed for different types of nitrogen. In Arab Heavy distillate, the total nitrogen gradually decreases in the order AHF-I(3.24), AHF-II(3.08) and AHF-III(2.97). A similar trend is observed for total nitrogen in the similar fractions from Arab Medium distillate. On the contrary, the total basic nitrogen in Arab Heavy fractions decreases from AHF-III (1.81) to AHF-I(1.66) to AHF-II(1.04). A similar trend is also observed for total basic nitrogen in three fractions of Arab Medium distillates. The strong basic nitrogen has a trend similar to that of total nitrogen in both Arab Heavy and Arab Medium fractions. In Arab Heavy, it gradually decreases from AHF-I(1.17) to AHF-II(0.72) to AHF-III(0.32). The weak basic nitrogen

in both distillates decreases and has a trend similar to that found for total basic nitrogen. In Arab Heavy, the weak basic nitrogen decreases from AHF-III(1.49) to AHF-I(0.49) to AHF-II(0.32). The strong basic nitrogen types represent compounds like pyridines, quinolines, benzoquinolines and higher benzologs. The weak basic nitrogen compounds include amides, aromatic amines and diaza compounds. The nonbasic nitrogen compounds are pyrroles, indoles, carbazoles and higher benzologs. This method determined the amounts of bases of differing pKa values that are present in the samples. Although these titrations did not provide any clearcut information about the molecular structures of the titrated species. However, by comparison with titration results of model nitrogen compounds in similar solvent systems, structural information about the bases titrating at various pKa values may be infered.

5.9.3.1 CORRELATION OF NONAQUEOUS POTENTIOMETRIC TITRATION DATA AND QUANTITATIVE INFRARED ANALYSIS RESULTS

The amount of different compound types were determined by nonaqueous potentiometric titration as well as by quantitative infrared spectroscopy. The data obtained by these two methods are compared in Table 31. The titration data is in terms of weight percent of fraction as taken from Table 30. The infrared data is taken from Table 29 and reproduced as weight percent of total fraction. Table 31 shows that the amount of strong, weak and nontitratable (nonbasic) compounds determined by nonaqueous potentiometric titration can be related quantitatively to those determined from infrared method. In case of

TABLE 31

COMPARISON OF NONAQUEOUS POTENTIOMETRIC TITRATION DATA AND QUANTITATIVE INFRARED ANALYSIS RESULTS

FRACTION	WEIGHT PERCENT OF FRACTION					
	STRONG BASES FROM		WEAK BASES FROM		NONTITRATABLE FROM	
	NAPT	IR	NAPT	IR	NAPT	IR
ARAB HEAVY						
AHF-I	35.9	40	15.0	12	49.1	48
AHF-II	23.5	27	10.3	9	66.2	64
AHF-III	10.6	_	50.2	76	39.2	24
ARAB MEDIUM						
AMF-I	32.5	46	10.0	12	57.5	42
AMF-II	15.8	18	7.9	7	76.3	75
AMF-III	8.7	_	42.7	75	48.6	25

fraction-I and fraction-II, the values obtained from two methods compared reasonably. In case of AHF-III and AMF-III, the infrared method showed only weak and nonbasic compounds whereas the titration results also indicates the presence of strong bases. This is due to the reason that the infrared spectra of fraction-III are not well resolved and the absorption bands for other compound types are overlapped by the broad absorption bands present in these spectra. The data presented in Table 31 further indicate that titration and infrared methods are reliable techniques to determine the type and amount of major compound types present in high-boiling distillates and residues of petroleum.

Comparison of data obtained from infrared analysis and the nonaqueous potentiometric titration led to the following conclusions.

1. Quantitative infrared spectroscopy can be used to estimate the type and amount of different compound types present in polar materials of high-boiling distillates.
2. Nonaqueous potentiometric titration can be employed for the qualitative and quantitative determination of compound types in polar material of high-boiling distillates.
3. Quantitative determination of compound types in polar fractions by infrared analysis can be compared to the similar data produced by nonaqueous potentiometric titration of these samples.

5.9.4 GAS CHROMATOGRAPHY OF HPLC FRACTIONS

Gas chromatographic analysis of petroleum fractions was carried out in order to characterize individual compounds on the basis of their

retention times. For this purpose, a number of model nitrogen compounds were subjected to gas chromatographic analysis to determine their retention times and their relative responses. The retention times of the model nitrogen compounds are given in Table 32 along with their boiling/melting points and molecular weights. As expected, it was found that the retention times are dependent on boiling points and molecular weights of the compounds. Generally, higher the boiling point, more time it will take from the column to elute and therefore higher will be its retention time. High molecular weight compounds are eluted later than the low molecular weight compounds and so their retention time will be higher. However, there are a few exception. The response of each compound was calculated by dividing the mass of nitrogen present in the compound by the area of the peak for that compound (113). The values obtained were normalized with respect to quinoline which was given a response value of 1.0. Response is the sensitivity of a detector for a compound containing an specific element. e.g. nitrogen phosphorus detector is specific for compounds containing nitrogen and phosphorus. Response of a detector for a compound having certain element is exhibited by the area of the peak produced for that compound. For equal concentration of two compounds, greater peak area means greater response and vice versa. Table 32 also shows the response values for different types of nitrogen compounds. Greater response was observed for low molecular weight compounds and whereas high molecular weight compounds exhibit lower response. e.g. Quinoline shows greater response than acridine but less than pyrrole. Similarly indole exhibit more response than carbazole. Cyclic compounds exhibit greater response than aromatics. This may be due to

TABLE 32

RETENTION TIME AND RESPONSE OF MODEL NITROGEN COMPOUNDS AS DETERMINED BY GAS CHROMATOGRAPHY

COMPOUNDS	RETENTION TIME(min)	RESPONSE	B.P/M.P °C	MOLECULAR WEIGHT
1-METHYL PYRROLE	2.00	1.30	114(L)	81.11
PYRROLE	2.05	1.05	130(L)	67.09
PYRROLIDINE	9.40	1.18	89(L)	71.12
QUINOLINE	17.40	1.00	238(L)	129.16
1-METHYL INDOLE	18.20	1.35	272(L)	131.18
INDOLE	19.00	1.06	254(S)	117.15
1,2,3,4-TETRA HYDROQUINOLINE	20.40	1.19	250(L)	133.20
PYRROLE 2-CARBOXYLIC ACID	22.00	1.20	192(S)	111.10
ACETANILIDE	24.00	0.92	304(S)	135.17
PHENAZINE	32.80	0.89	360(S)	180.20
CAFFEINE	35.00	0.87	237(S)	194.20
CARBAZOLE	35.40	1.04	355(S)	167.21
PHENANTHRIDINE	36.00	0.95	349(S)	179.22
ACRIDINE	39.00	0.97	346(S)	179.22
IMIDAZOLE	43.60	1.13	257(S)	68.08

the reason that cyclic compounds are less stable and are easily and completely converted to cyano radicals as compared to more stable aromatics. e.g. higher response is observed for 1,2,3,4-tetrahydroquinoline as compared to quinoline. Compounds having two nitrogen atoms showed less response than similar compounds with one nitrogen atom. This is obviously due to the reason that all the nitrogen in diaza compound is not converted to cyano radicals. e.g. phenazine exhibited decreased response than acridine and phenanthridine. The effects of substitution and saturation of nitrogen compounds on the detector response are shown in Table 33. The response are relative to unity for the parent compounds. It is observed that the saturation and alkyl substitution in the ring increase the response of a nitrogen compound. e.g. 1-methylpyrrole has a response factor of 1.24 as compared to pyrrole (1.00). Similarly, 1,2,3,4-tetrahydroquinoline (1.19) shows greater response than quinoline (1.00). The nitrogen phosphorus detector(NPD) was checked for its selectivity and sensitivity to nitrogen compounds. The selectivity and sensitivity of the detector is illustrated in Figure 22 which shows a chromatogram obtained for a blend of naphthalene and quinoline. The selectivity (gC/gN) is the ratio of weights of carbon and nitrogen in gram for equal response of the detector (i.e. producing peaks of equal areas for both elements). The selectivity of this detector was calculated to be 1.97×10^4. It means that if a sample contains mass of carbon and nitrogen in the ratio of 1.97×10^4:1 grams, the detector will show equal response for the two elements and will produce peaks of equal areas.

The NPD also gives good response to phosphorus when it is

TABLE 33

EFFECT OF ALKYL SUBSTITUTION IN NITROGEN COMPOUNDS ON THE DETECTOR RESPONSE

COMPOUNDS	RESPONSE
PYRROLE*	1.00
1-METHYL PYRROLE	1.24
PYRROLE 2-CARBOXYLIC ACID	1.14
PYRROLIDINE	1.12
IMIDAZOLE	1.00
INDOLE*	1.00
1-METHYL INDOLE	1.27
CARBAZOLE	1.00
QUINOLINE*	1.00
1,2,3,4-TETRA HYDROQUINOLINE	1.19
ACRIDINE	0.97
PHENANTHRIDINE	0.95
PHENAZINE	0.89

* INDICATES PARENT COMPOUNDS

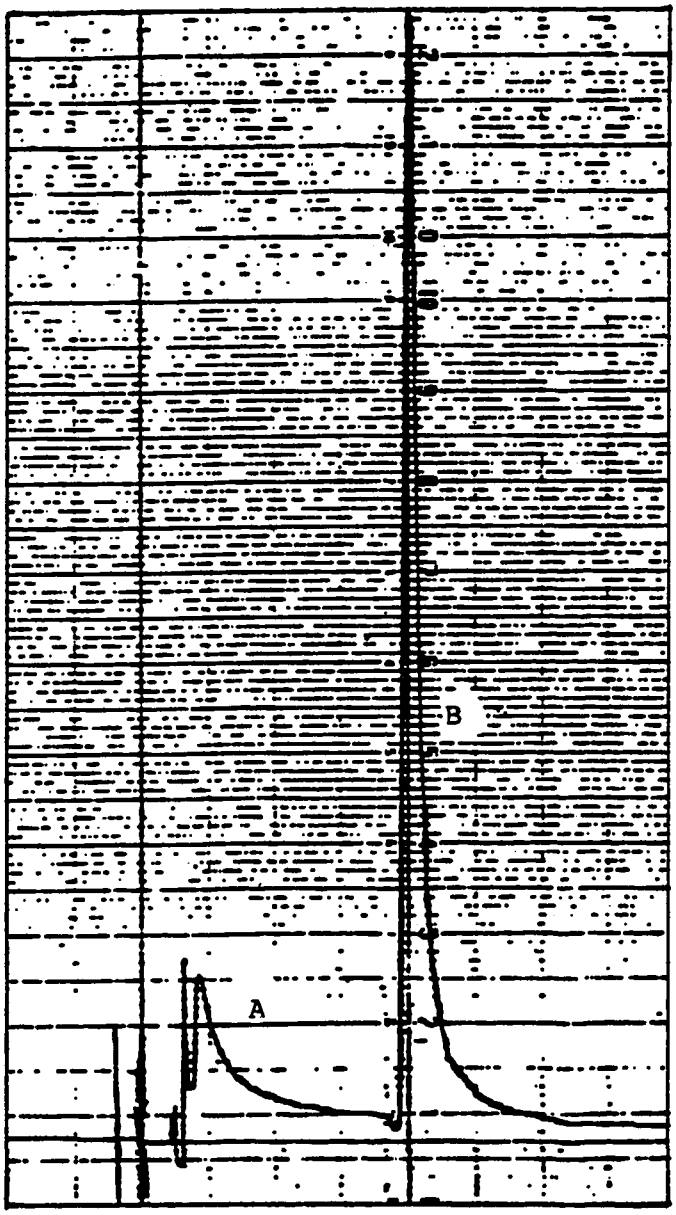


Figure 22. Gas Chromatogram of a Mixture of Naphthalene(A) and Quinoline(B) in 1,2-Dichloroethane. Quinoline was 25 ppm (2.71 ppm Nitrogen) and Naphthalene 17400 ppm (16300 ppm Carbon)

operated in nitrogen mode. However, the phosphorus contents of petroleum are known to be in negligible amount (113) and therefore, NPD response to phosphorus can be ignored.

The response of the NPD was found approximately proportional to the nitrogen content of a compound but it also depends on the structure of the compounds. The detector mechanism is based on the formation of cyano radicals in a cool flame zone (111). In general, compounds having structure favorable for the production of more cyano radicals are expected to give greater response.

A synthetic mixture of nine pure nitrogen compounds was prepared and chromatographed. The chromatogram obtained for this mixture is shown in Figure 23. A satisfactory separation was achieved for the mixture and the compounds were eluted in reasonable time.

The petroleum samples were chromatographed under the similar conditions. The chromatograms are given in Figure 24 through 29. A number of peaks were observed in these chromatograms of six fractions. The separation of different compounds, however, was not very effective. This may be due to the extreme complexity and high boiling points of the samples that all components did not elute completely through the column at the operating temperature. Table 34 shows the compounds identified on the basis of their retention times in six HPLC fractions. The discussion on the nitrogen compounds identified in each fraction is given in the following section. These nitrogen compounds were identified by comparing the retention times of the peaks appeared in the chromatograms of the HPLC fractions with those obtained for the

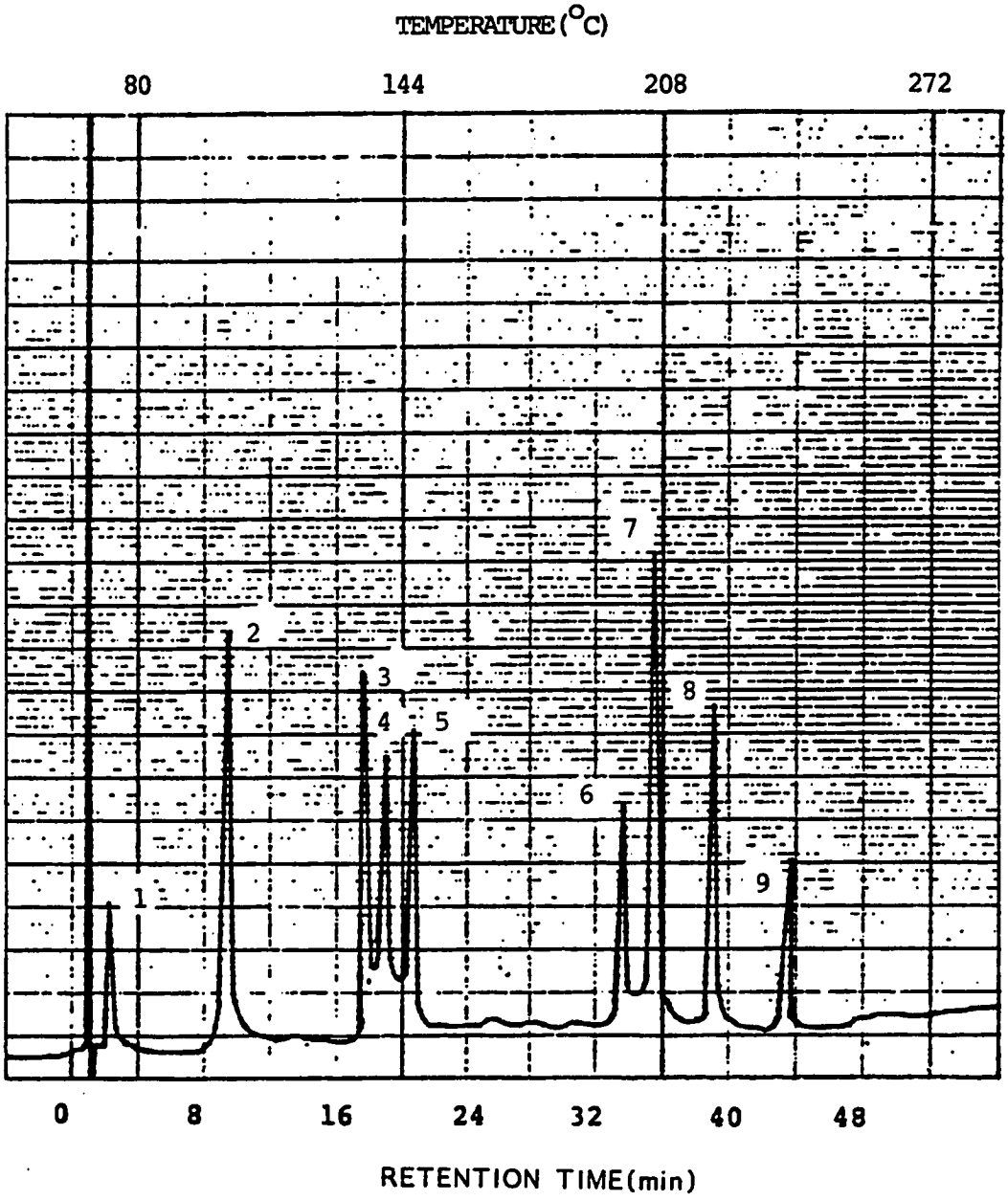


Figure 23. Gas Chromatogram of a Synthetic Mixture of Nine Pure Nitrogen Compounds in 1,2-Dichloroethane. 1. 1-Methylpyrrole, 2. Pyrrolidine, 3. Quinoline, 4. Indole, 5. 1,2,3,4-Tetrahydroquinoline, 6. Phenazine, 7. Caffeine, 8. Acridine, 9. Imidazole

TABLE 34

NITROGEN COMPOUNDS IDENTIFIED BY GAS CHROMATOGRAPHY

COMPOUNDS	AHF-I	AHF-II	AHF-III	AMF-I	AMF-II	AMF-III
QUINOLINE	X		X			
1-METHYL INDOLE		X				
INDOLE		X	X		X	X
1,2,3,4-TETRA HYDROQUINOLINE	X		X	X		X
PYRROLE 2-CARBOXYLIC ACID		X	X			X
PHENAZINE	X			X		
CAFFEINE			X			X
CARBAZOLE		X			X	
PHENANTHRIDINE	X			X		
ACRIDINE	X	X	X	X	X	
IMIDAZOLE		X	X			

X INDICATES THE PRESENSE OF COMPOUND IN A FRACTION

model nitrogen compounds.

The gas chromatogram obtained for AHF-I fraction is shown in Figure 24. Six well defined peaks were obtained in this chromatogram. The retention times of these peaks were compared with the retention times of model nitrogen compounds. Five nitrogen compounds were identified which are of the pyridine type. These compounds are quinoline, 1,2,3,4-tetrahydroquinoline, phenazine, phenanthridine and acridine. The molecular weight of these compounds were in the range 129-180 amu. The compound eluted at peak number 3 could not be positively identified. Among the nitrogen compounds identified, phenazine and acridine appeared to be the major compounds present in this fraction. The results from quantitative infrared study and potentiometric titration of this fraction indicate pyridine type compounds to be the major component of this fraction. Similarly, the ultraviolet spectroscopic results show this fraction to be mainly consists of substituted benzoquinolines and benzoisoquinolines which are pyridine type compounds. Therefore, it can be said positively that the fraction AHF-I mainly contains pyridine type nitrogen compounds.

The gas chromatogram of AHF-II fraction shown in Figure 25 contained eleven peaks. Six nitrogen compounds were identified in this fraction which are mostly of the pyrrole type. These compounds are 1-methylpyrrole, indole, pyrrole-2-carboxylic acid, carbazole, acridine and imidazole. The molecular weights of these compounds range from 68 to 179 amu. The peak area of indole and carbazole is more and thus these compounds appeared to be in greater amount as compared to other nitrogen compounds identified in this fraction. Some of the peaks could

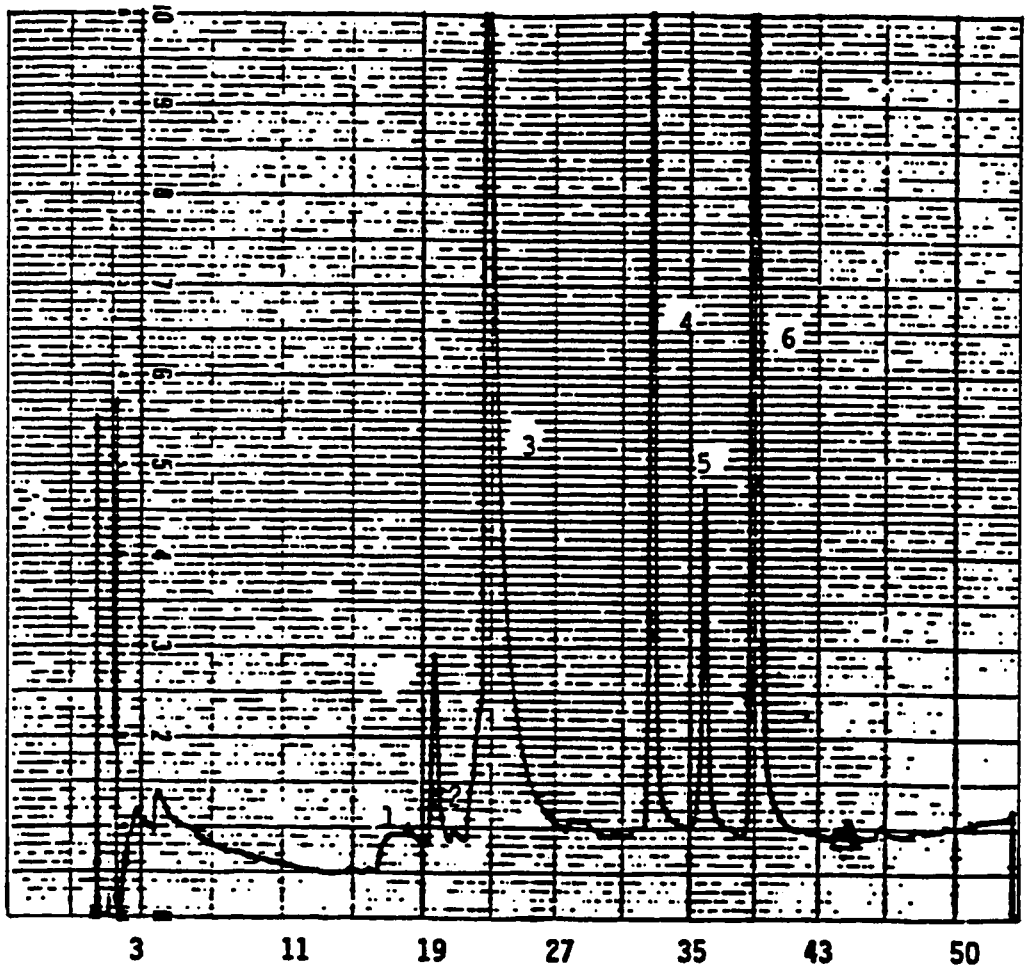


Figure 24. Gas Chromatogram of AHF-I Fraction. The Compounds Identified are

1. Quinoline
2. 1,2,3,4-Tetrahydroquinoline
4. Phenazine
5. Phenanthridine
6. Acridine

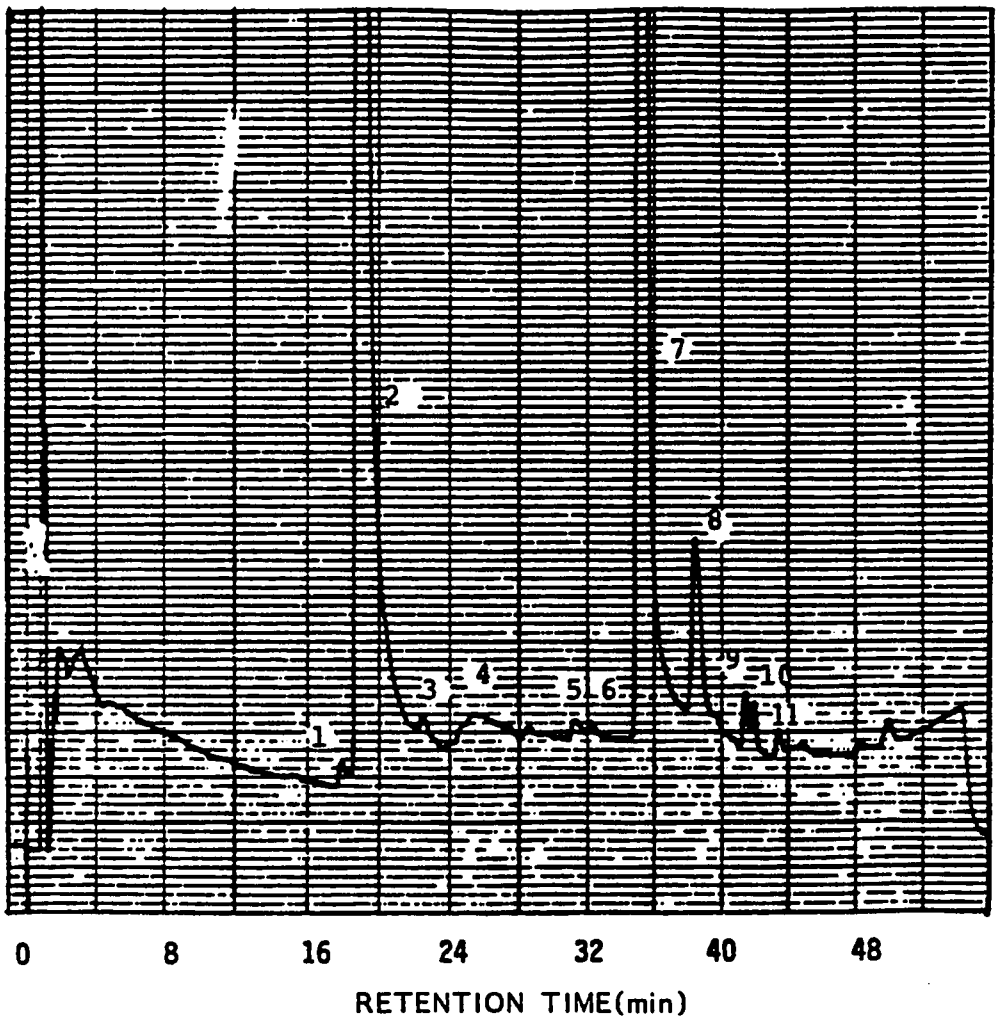


Figure 25. Gas Chromatogram of AHF-II Fraction. The Compounds Identified are

1. 1-Methylindole
2. Indole
3. Pyrrole-2-Carboxylic Acid
7. Carbazole
8. Acridine and
11. Imidazole

not be identified. The quantitative infrared compound type analysis showed that this fraction contain mainly pyrrole type compounds. Similarly, potentiometric titration data showed that a major portion of this fraction consists of nonbasic components. In acetic anhydride:benzene (2:1) solvent system, pyrrolic type compounds were found nonbasic in nature. The total nitrogen data also indicate that this fraction contains mostly nonbasic nitrogen in the form of pyrrole type components. The ultraviolet spectroscopy results further suggest that this fraction consists of substituted carbazoles and other pyrrolic type compounds. All these information from various sources firmly indicate that the fraction AHF-II mainly comprises of pyrrole type nitrogen compounds.

The gas chromatogram of AHF-III fraction is shown in Figure 26. Eleven peaks were observed in this chromatogram whose retention times were compared with those of pure nitrogen compounds. This comparison led to identification of seven nitrogen compounds which are quinoline, indole, 1,2,3,4-tetrahydroquinoline, pyrrole-2-carboxylic acid, caffeine, acridine and imidazole. The molecular weights of these compounds were in the range 68-194 amu. Caffeine and acridine appeared to be in major quantities as shown by their peak areas. The peak number 5 in this chromatogram could not be identified and it also appeared as one of the major compounds. Caffeine is the only cyclic amide which was identified in this fraction. The infrared compound type analysis showed that about three-fourth of this fraction contains amide type compounds and the one fourth as phenols. The ultraviolet spectroscopic results suggest that this fraction contains amides besides other compounds

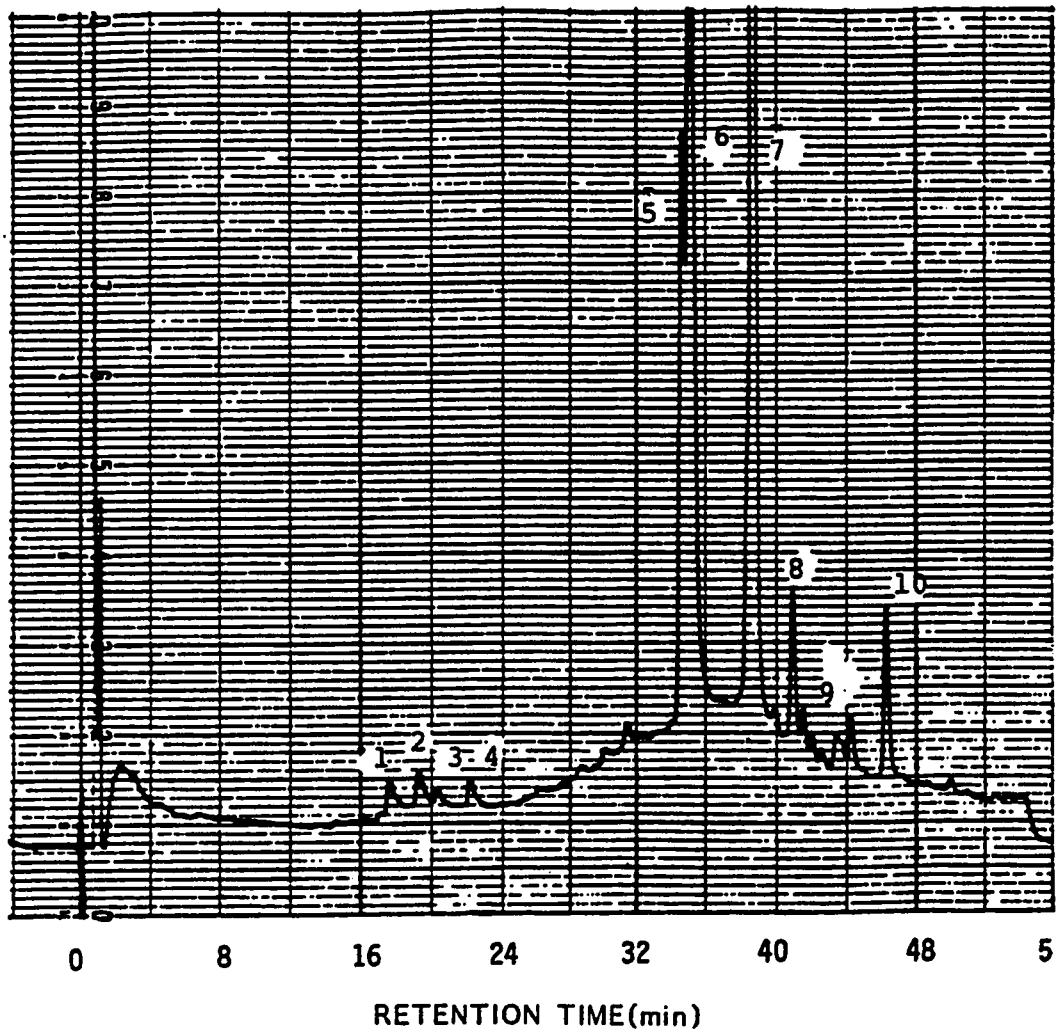


Figure 26. Gas Chromatogram of AHF-III Fraction. The Compounds Identified are

1. Quinoline
2. Indole
3. 1,2,3,4-Tetrahydroquinoline
4. Pyrrole-2-Carboxylic Acid
6. Caffeine
7. Acridine and
9. Imidazole

types present in it. The potentiometric titration data showed that the amides are the major constituents of this fraction. Amides were titrated as weak basic compounds. The weight percent of weak basic nitrogen was also high in this fraction. In acetic anhydride:benzene (2:1) solvent system, amide type compounds behaves as weak bases. Therefore, it can be concluded that the fraction AHF-III mainly consists of amide type nitrogen compounds.

The gas chromatogram of AMF-I fraction is shown in Figure 27 which shows six peaks. In this fraction, four nitrogen compounds were identified which are of the pyridine type. These compounds have also been identified in AHF-I fraction. These compounds are 1,2,3,4-tetrahydroquinoline, phenazine, phenanthridine and acridine. The molecular weights of these compounds range from 133 to 180 amu. Phenanthridine appeared to be in major amount among the nitrogen compounds identified in this fraction. The quantitative infrared study and potentiometric titration results of this fraction showed that pyridines are the main constituents of this fraction. Again, the ultraviolet spectroscopic results show that this fraction mainly consists of substituted benzoquinolines and benzoquinolines which are pyridine type compounds. The gas chromatographic analysis further support the results obtained from other techniques. Thus, the fraction AMF-I mainly contains pyridine type nitrogen compounds.

The gas chromatogram of AMF-II fraction shown in Figure 28 contained four prominent peaks. Three nitrogen compounds were identified in this fraction, two of which are of the pyrrole type. These compounds are indole, carbazole and acridine. The molecular weights of

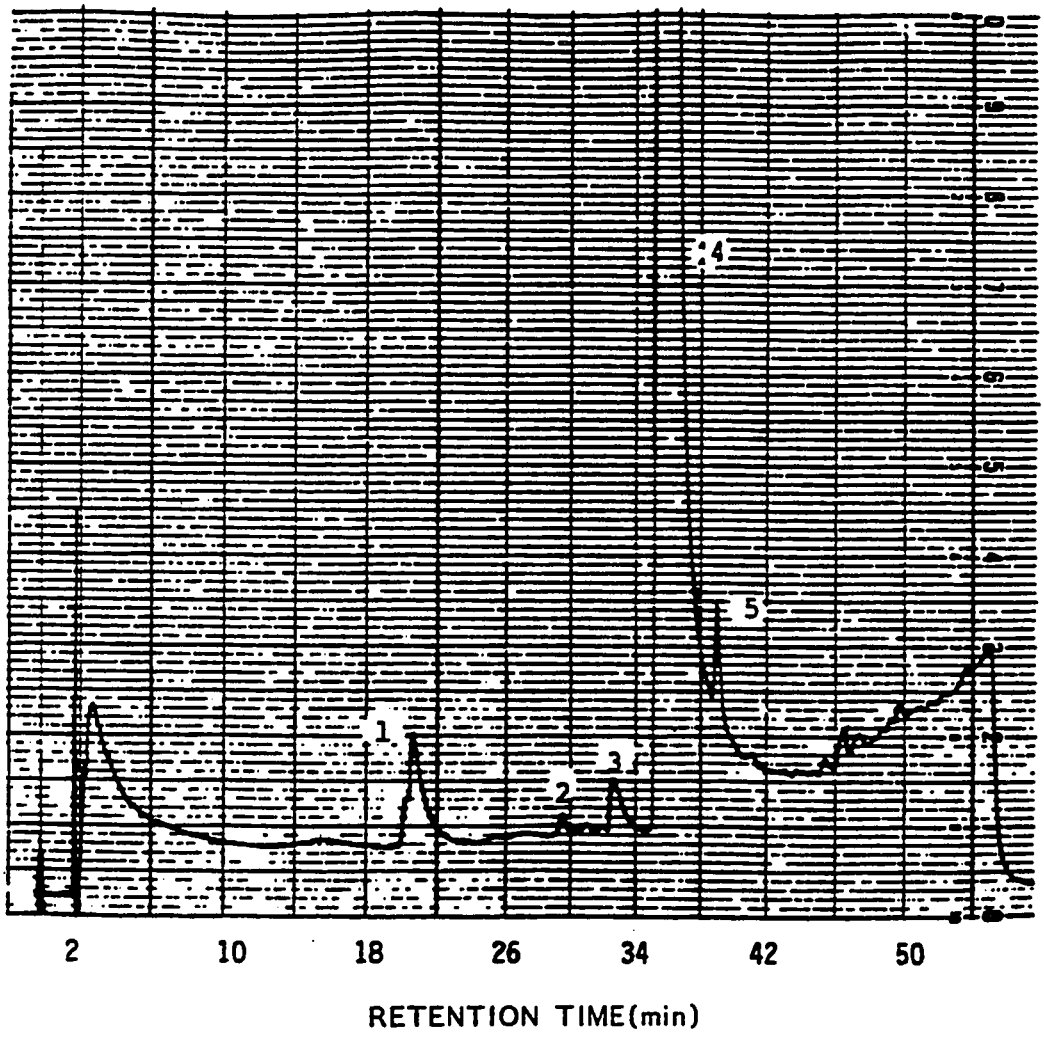


Figure 27. Gas Chromatogram of AMF-I Fraction. The Compounds Identified are

1. 1,2,3,4-Tetrahydroquinoline
3. Phenazine
4. Phenazine
5. Acridine

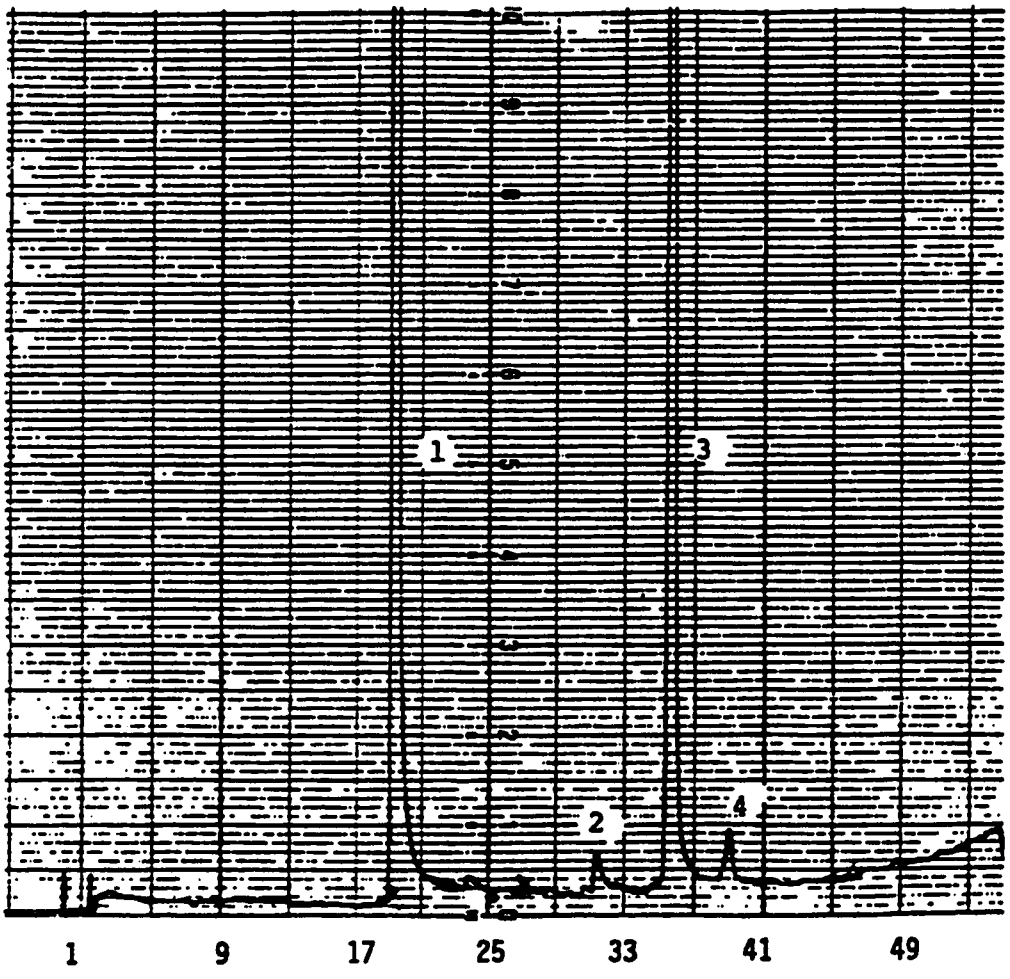


Figure 28. Gas Chromatogram of AMF-II Fraction. The Compounds Identified are

1. Indole
3. Carbazole
4. Acridine

these compounds were in the range 117-179 amu. The peak area of indole and carbazole compounds showed that they are in greater amount as compared to other nitrogen compounds identified in this fraction. Some of the peaks could not be identified. The infrared quantitative analysis showed that this fraction comprises mainly of pyrrole type compounds. Potentiometric titration data also showed this fraction to be mainly consists of nonbasic compounds. In acetic anhydride:benzene (2:1) solvent system, pyrrolic compounds behave nonbasic in character (101). The weight percent of nonbasic nitrogen present in this fraction indicate that it mostly contains nonbasic nitrogen which is in the form of pyrrole type compounds. The ultraviolet spectroscopy of this fraction further suggest that it consists of substituted carbazoles and other pyrrolic type compounds. Thus the fraction AMF-II appears to be predominantly pyrrole type nitrogen compounds.

The gas chromatogram of AMF-III fraction is shown in Figure 29. Nine well resolved peaks were observed in this chromatogram whose retention times were compared with those of pure nitrogen compounds. As a result of this comparison, four nitrogen compounds were identified which are indole, 1,2,3,4-tetrahydroquinoline, pyrrole-2-carboxylic acid and caffeine. The molecular weights of these compounds range from 111 to 194 amu. The components at peak number 4 and 9 are in major quantities as evidenced from their peak areas. The component at peak number 9 could not be identified positively. Caffeine appeared to be the component in major quantity among the identified nitrogen compounds and it is the only amide type compound identified. Other compounds identified are of pyridine and pyrrole types. The

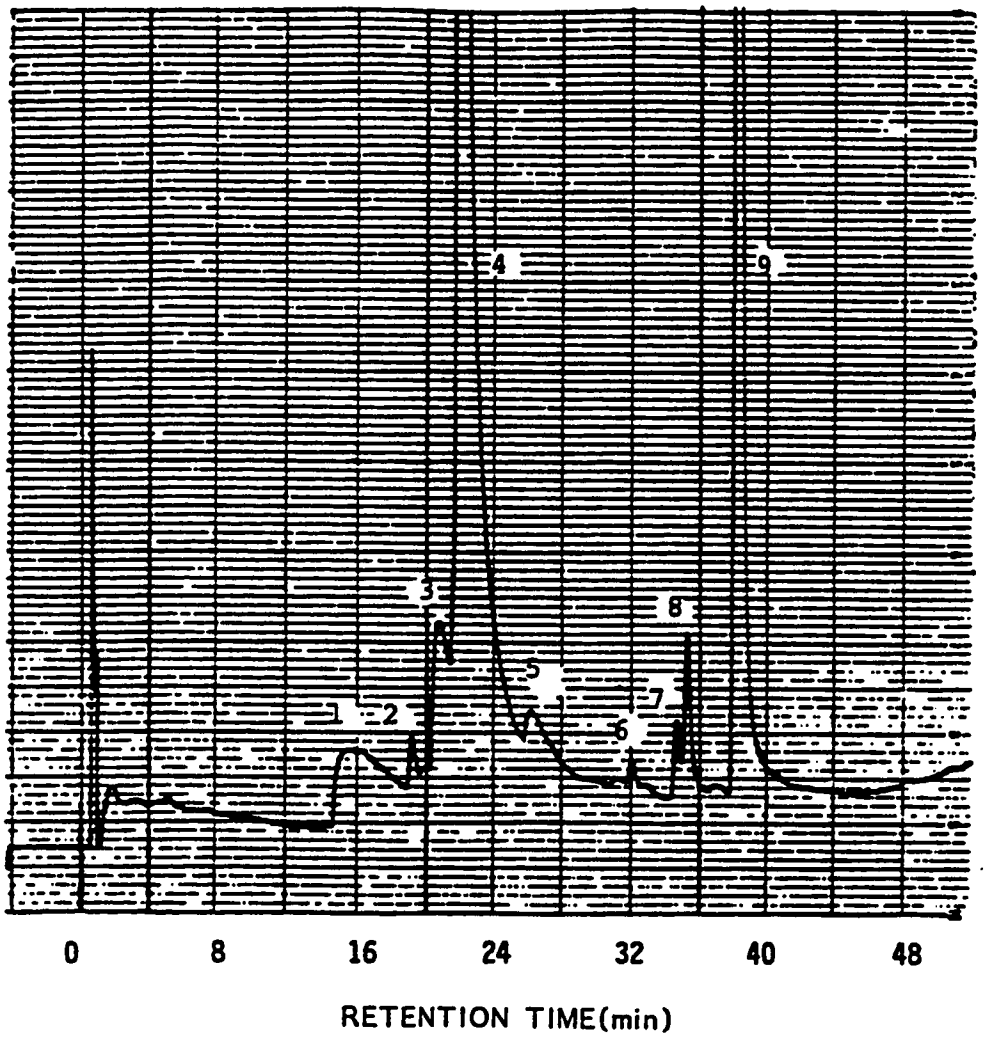


Figure 29. Gas Chromatogram of AMF-III Fraction. The Compounds Identified are

2. Indole
3. 1,2,3,4-Tetrahydroquinoline
4. Pyrrole-2-Carboxylic Acid
8. Caffeine

quantitative infrared study indicates that amides are present in this fraction as major compound types along with phenols. The fact that other compound types were not detected was due to the poor resolution of infrared bands present in this fraction. The qualitative ultraviolet spectroscopy indicates that this fraction contains amides as major compound types besides other compounds. Titration results are also in agreement with other studies. The potentiometric titration results showed that the amides are the major constituents of this fraction. Moreover, the weight percent of weak basic nitrogen was found more in this fraction. In acetic anhydride:benzene (2:1) solvent system, amide type compounds were titrated as weak basic in nature. Therefore, the fraction-III mainly contains amide type nitrogen compounds.

5.9.5 GAS CHROMATOGRAPHY-MASS SPECTROMETRY OF HPLC FRACTIONS

All of the six HPLC fractions obtained from chromatography of Arab Heavy and Arab Medium nitrogen concentrates were analyzed by combined gas chromatography-mass spectrometry. A concentrated solution of each fraction prepared in 1,2-dichloroethane was injected into the gas chromatograph for further separation and identification based on both gas chromatograph and mass spectrometer instruments. The procedure used resulted in the identification of large number of compounds along with many aromatics and a few alkane type components. Mass spectral identification of these components was based on the computer library search, literature spectra and on the extrapolation of some of the features of the literature spectra to the spectra encountered in this work. Some of the spectra appeared to

contain more than one component. This was due to incomplete separation of various components in gas chromatograph. Due to this reason, the spectra recorded for one component also showed the intensity peaks of other components. In such cases, identification was based on the characteristic homologs ion series present in the spectra. The total ion chromatograms (TIC) for the six HPLC fractions are reproduced in Figure 30 through 35. The nitrogen compounds identified are listed in Table 35 along with their molecular weights. The components of each fraction as appeared in the total ion chromatograms were identified by matching their mass spectra with those of the standard mass spectra of pure nitrogen compounds available in the literature (110). A large number of mass spectra could not be identified because of the limited availability of mass spectra of polyaromatic nitrogen compounds in the literature which were expected to be present in these fractions. Besides, presence of background peaks in the mass spectra of the separated components made the characterization further difficult.

The total ion chromatogram obtained for AHF-I fraction is shown in Figure 30. Several peaks are observed and the separation of the components appears to be good. Only two nitrogen compounds were, however, positively identified as 1-cyano,3-methylisoquinoline and 1-naphthylisocyanate at scan numbers 575 and 759 respectively. Their mass spectra are given in Figures 30a and 30b along with mass spectra of pure compounds respectively. Each of these compounds may exist in several isomeric forms which have similar mass spectra. The identification of other compounds was difficult because they were found to contain background peaks due to incomplete separation of the

TABLE 35

NITROGEN COMPOUNDS IDENTIFIED BY

GAS CHROMATOGRAPHY-MASS SPECTROMETRY

	NAME OF THE COMPOUND	MOL. WEIGHT
1.	1-CYANO,3-METHYLISOQUINOLINE	168
2.	1-NAPHTHYLISOCYANATE	169
3.	CARBAZOLE	167
4.	2-HYDROXYQUINOLINE	145
5.	INDAZOLE	118
6.	5-METHYLINDOLE	131
7.	INDOLE	117
8.	BENZOQUINOLINE/BENZOISOQUINOLINE	179
9.	1-CYANOISOQUINOLINE-2-OXIDE	170
10.	5,7-DIMETHYL-OCTAHYDRO-INDOLIZINE	153
11.	N-N-BUTYLPYRROLE	123
12.	2,6-DIMETHYLAMINOPYRIMIDINE	123
13.	ISOBUTYRAMIDE	87
14.	N-PHENYLDIACETAMIDE	135
15.	CAFFEINE	194

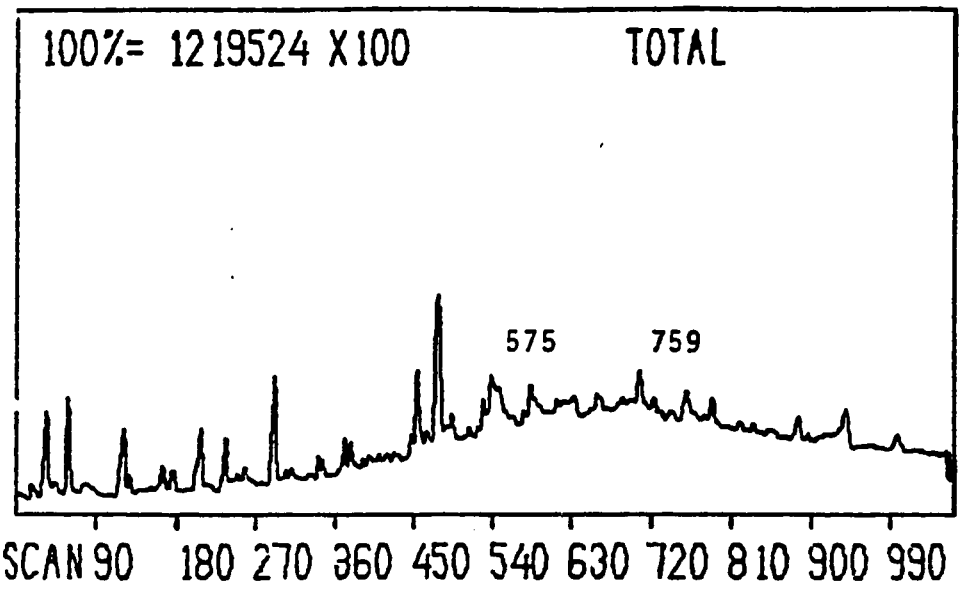
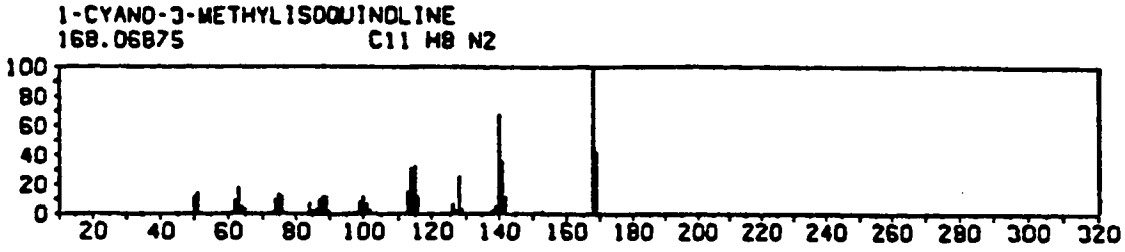


Figure 30. Total Ion Chromatogram of AHF-I Fraction



AHF-I SCAN NUMBER 575

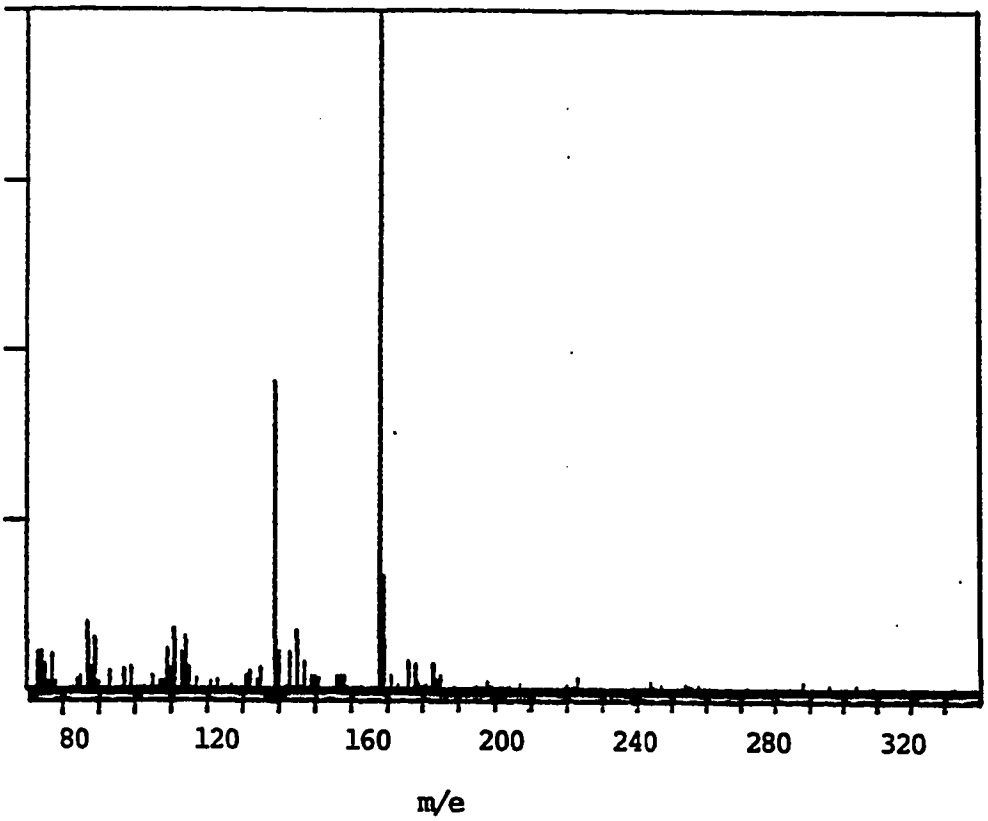
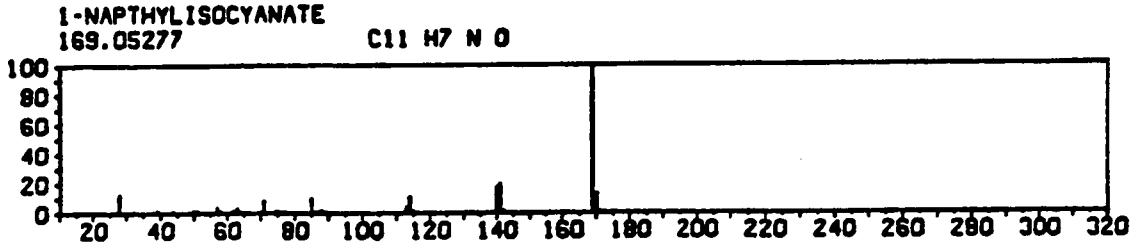


Figure 30a. Mass Spectrum of a Compound obtained from AHF-I Fraction compared with Mass Spectrum of pure 1-Cyano-3-Methylisoquinoline



AHF-I SCAN NUMBER 759

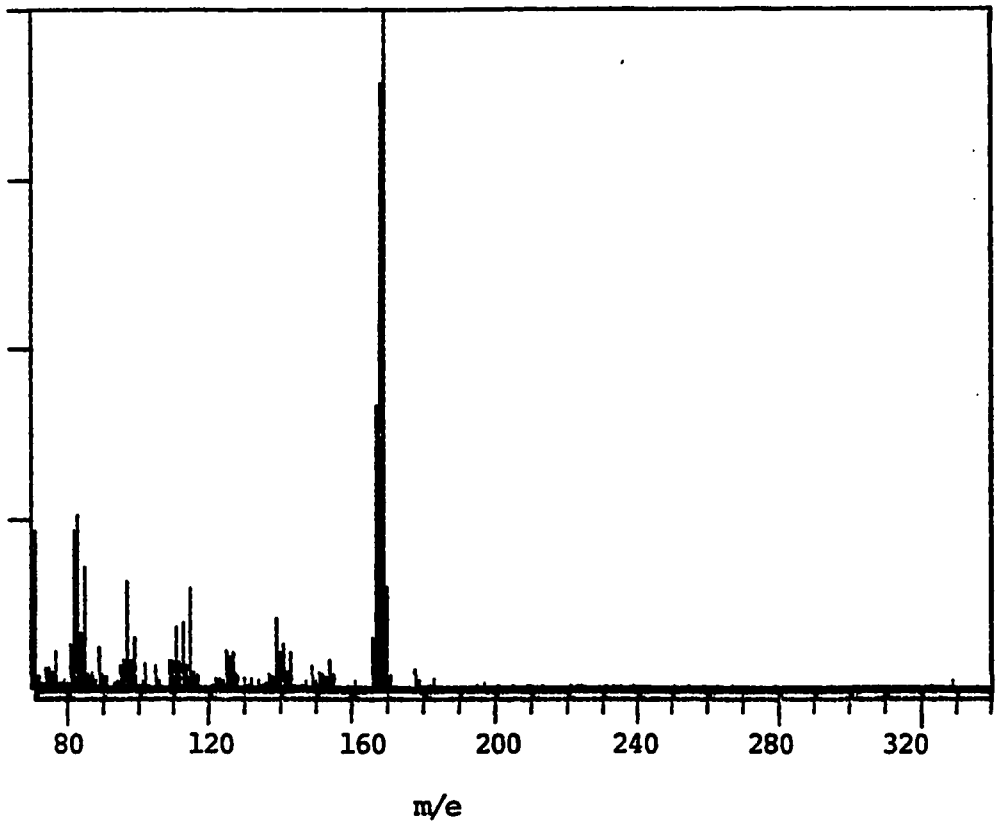


Figure 30b. Mass Spectrum of a Compound obtained from AHF-I Fraction compared with Mass Spectrum of pure 1-Naphthylisocyanate

components. The library search did not produce a positive identification, therefore the remaining spectra could not be assigned to specific compounds. This fraction also shows many spectra for combination of condensed aromatics and saturated acids as indicated by the presence of characteristic homologs ion series of phenylalkane (m/e 77,91,105,119,133,.....) and alkanes (m/e 71,85,99,113,127, 141,.....) both normal and branched.

The total ion chromatogram (TIC) obtained for AHF-II fraction is shown in Figure 31. A number of peaks are observed in this chromatogram. Six nitrogen compounds were identified in this fraction by matching their mass spectra with those of pure compounds. Most of these compounds are of the pyrrole type. The compounds identified are carbazole(357), 2-hydroxyquinoline (746), Indazole(820), 5-methylindole (874), Indole(1140) and Benzoquinoline/Benzoisoquinoline (1516). The values given within the parenthesis against the compounds are the scan numbers at which these compounds were identified. Their mass spectra are reproduced in Figures 31a through 31f along with mass spectra of pure compounds. Other mass spectra show fragment ions which are characteristic of aromatic hydrocarbons. Overlapping of components was also noticed as indicated by the presence of characteristic fragments and molecular ions belonging to other compounds. Some of the nitrogen compounds appeared at two different scan numbers. This may be due to the presence of isomers in this fraction.

The total ion chromatogram obtained for AHF-III fraction is shown in Figure 32. The chromatogram shows a number of peaks of separated components. Two nitrogen compounds were identified in this fraction.

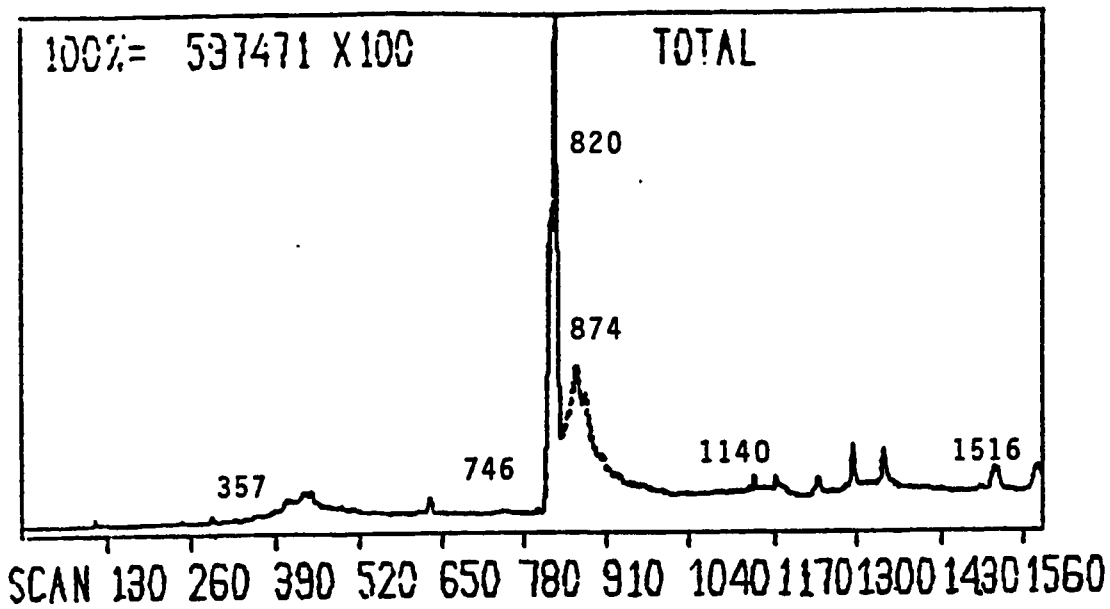
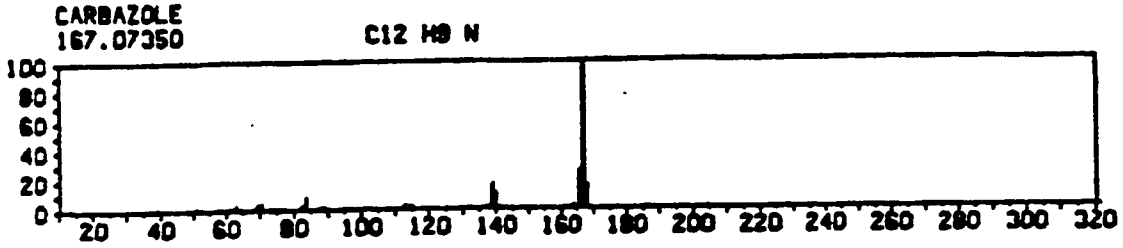


Figure 31. Total Ion Chromatogram of AHF-II Fraction



AHF-II SCAN NUBMER 357

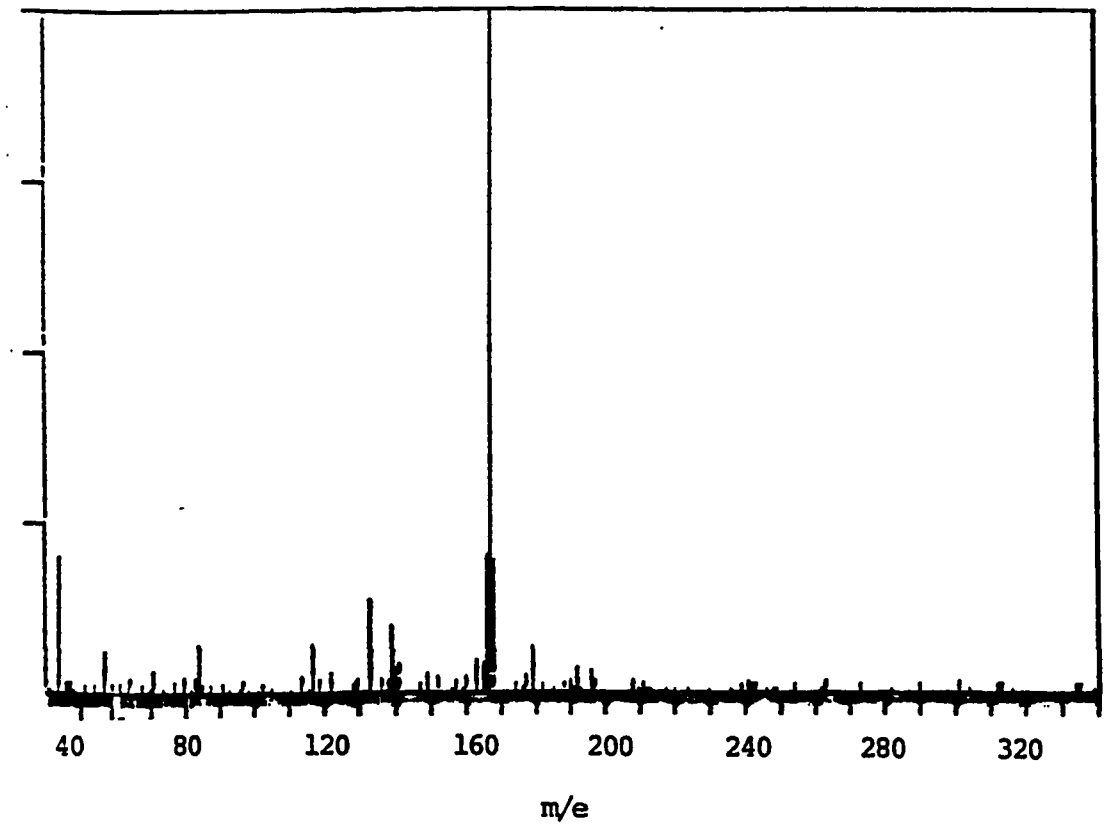
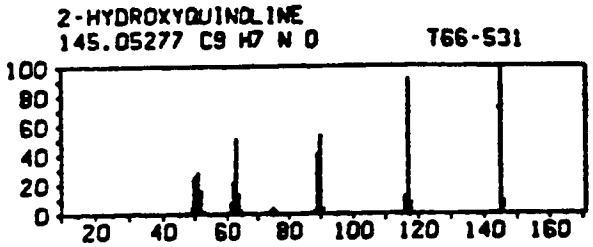


Figure 31a. Mass Spectrum of a Component obtained from AHF-II Fraction compared with Mass Spectrum of pure Carbazole



AHF-II SCAN NUMBER 746

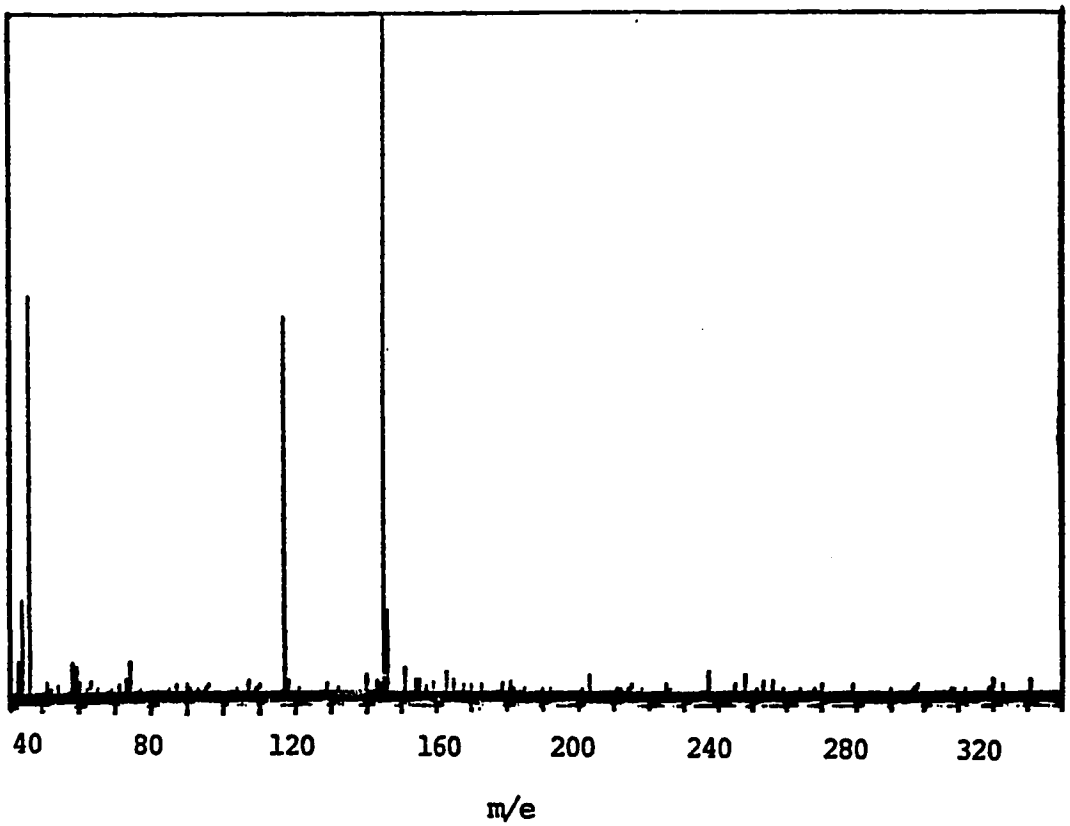
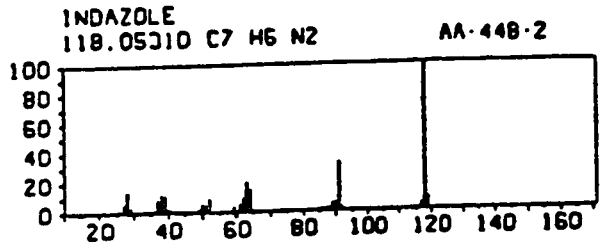


Figure 31b. Mass Spectrum of a Component obtained from AHF-II Fraction compared with Mass Spectrum of pure 2-Hydroxyquinoline



AHF-II SCAN NUMBER 820

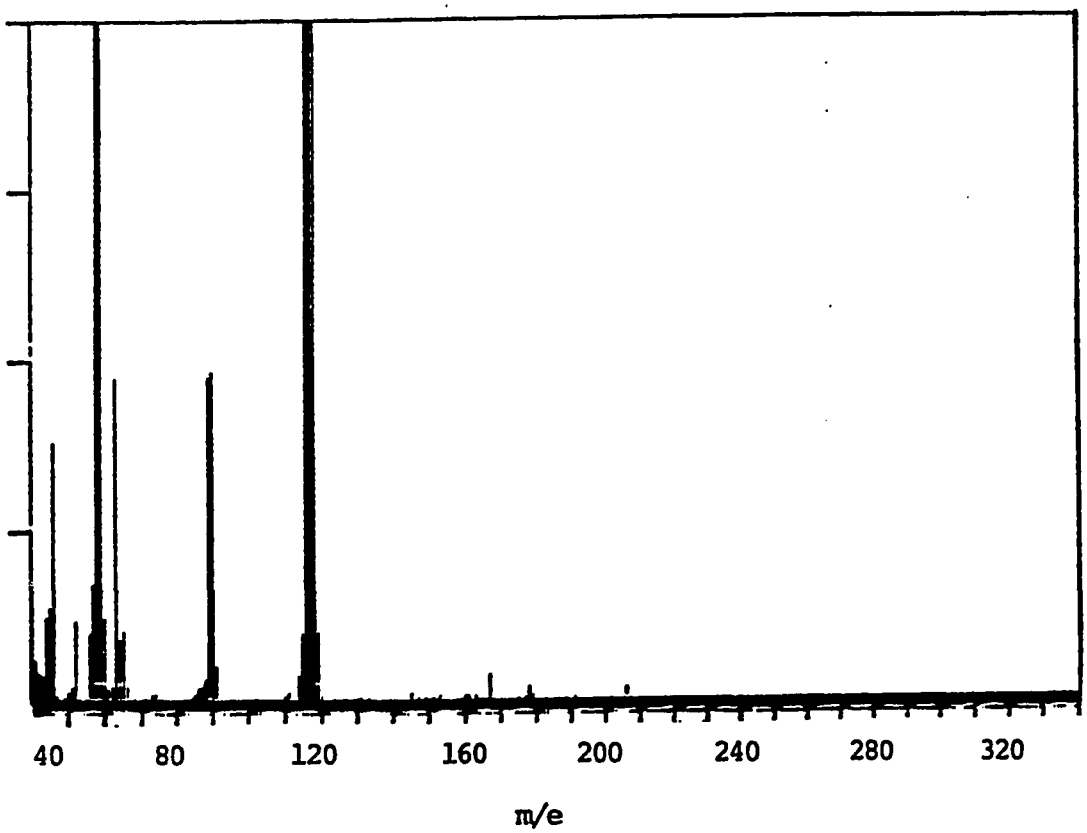
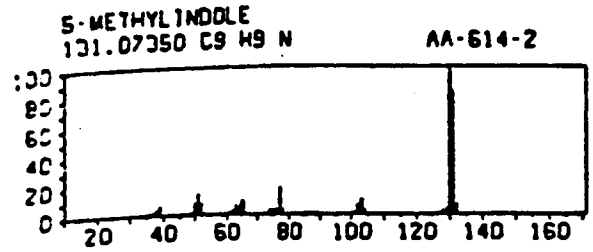


Figure 31c. Mass Spectrum of a Component obtained from AHF-II Fraction compared with Mass Spectrum of pure Indazole



AHF-II SCAN NUMBER 874

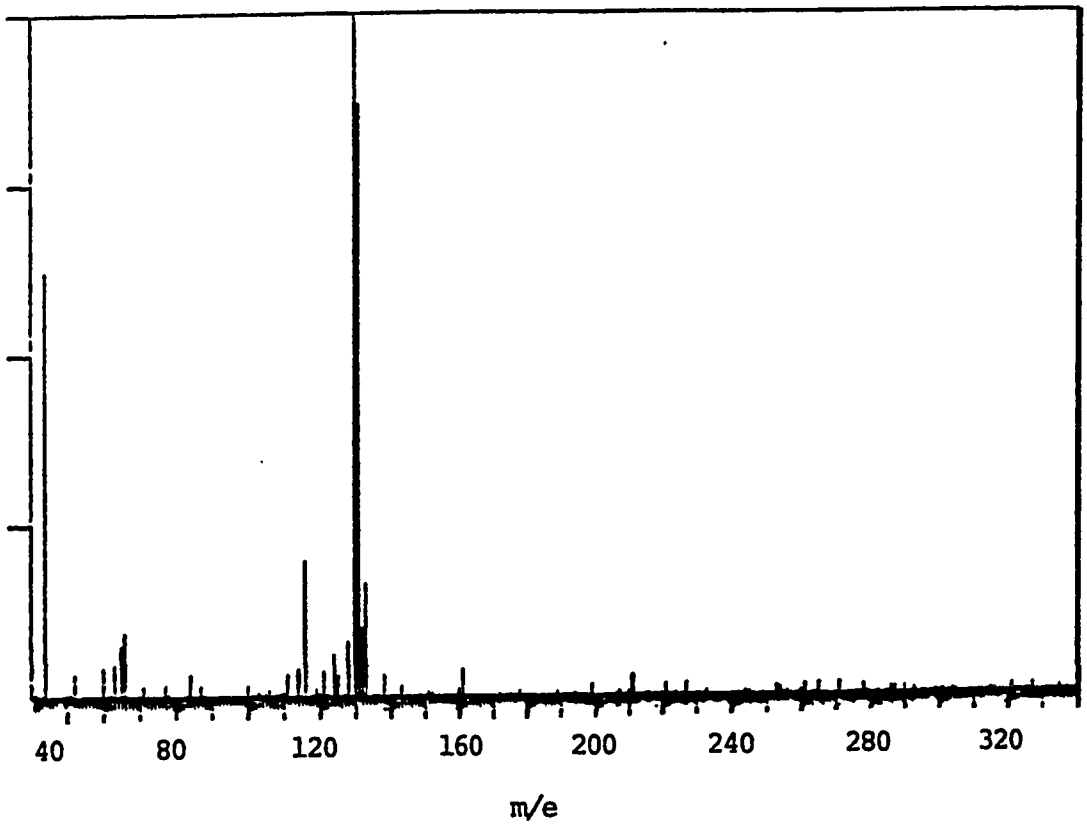
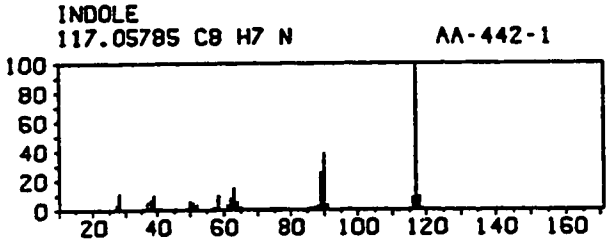


Figure 31d. Mass Spectrum of a Component obtained from AHF-II Fraction compared with Mass Spectrum of pure 5-Methylindole



AHF-II SCAN NUMBER 1140

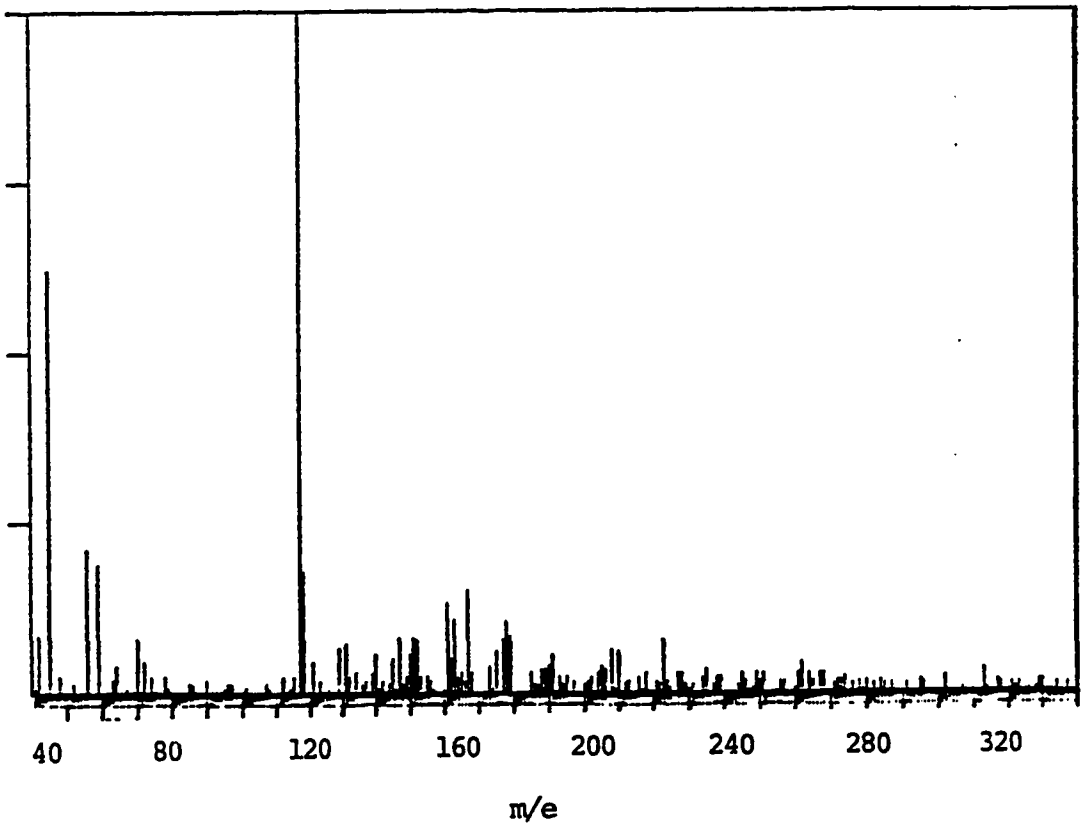


Figure 31e. Mass Spectrum of a Component obtained from AHF-II Fraction compared with Mass Spectrum of pure Indole

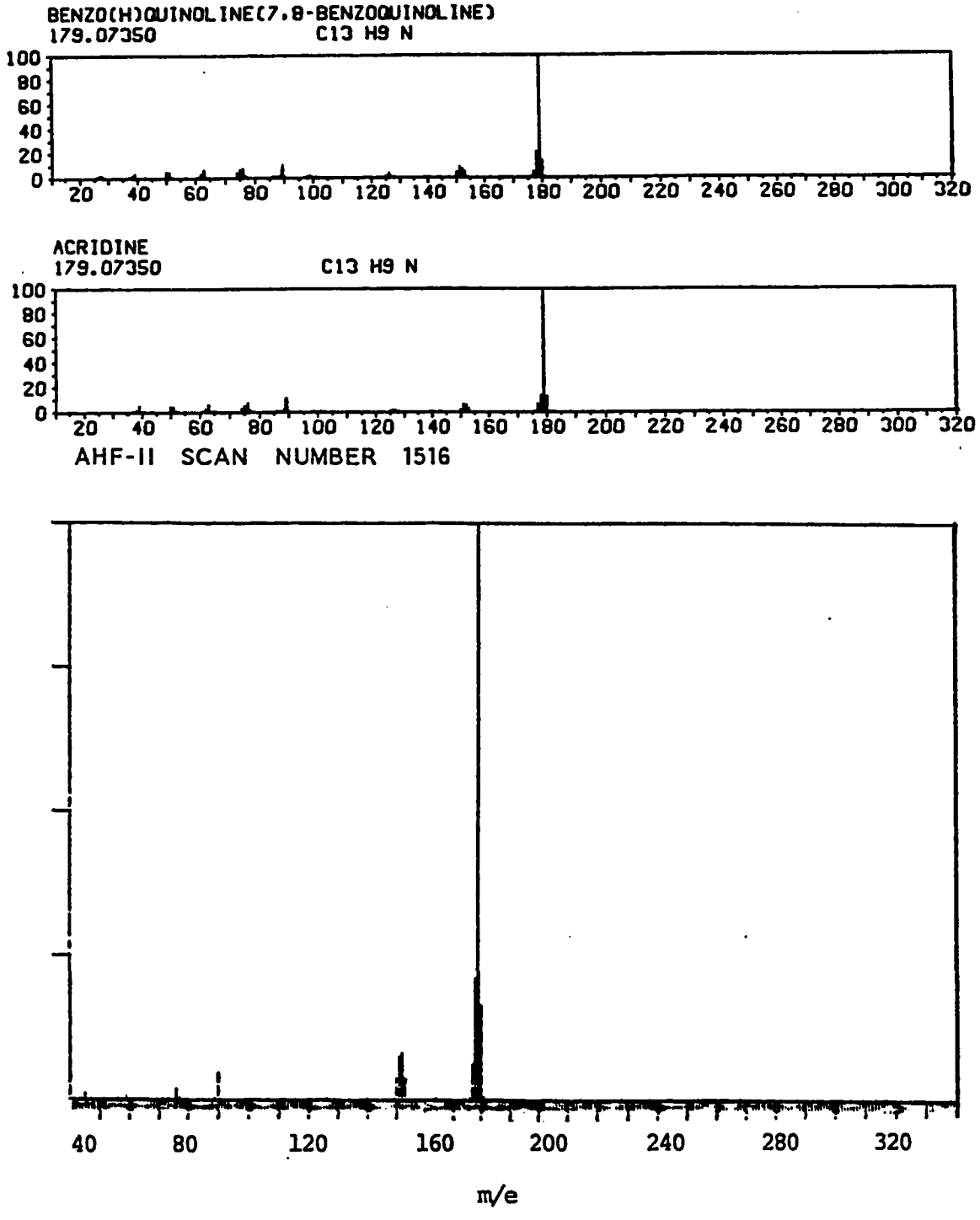


Figure 31f. Mass Spectrum of a Component obtained from AHF-II Fraction compared with Mass Spectra of pure Acridine and 7,8-Benzoquinoline

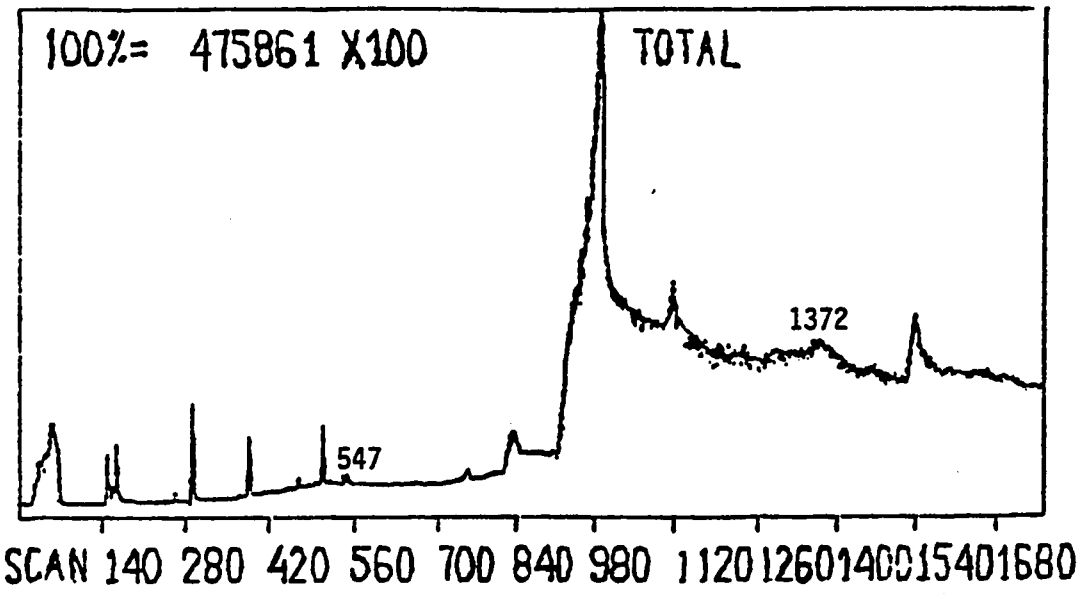
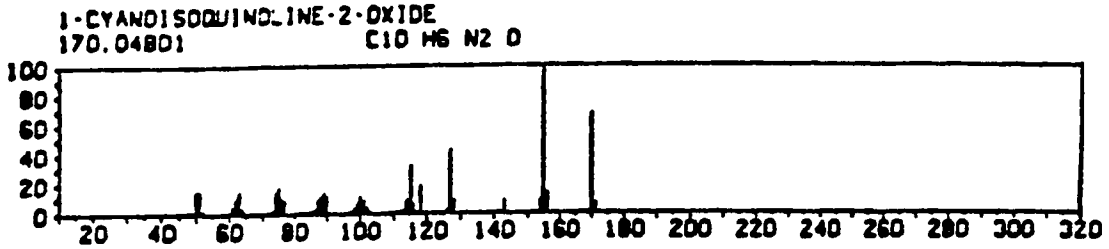


Figure 32. Total Ion Chromatogram of AHF-III Fraction

The compounds identified are 1-cyanoisoquinoline-2-oxide and carbazole at 547 and 1372 scan numbers respectively. The mass spectra obtained are given in Figures 32a and 32b along with mass spectra of pure compounds. Some other mass spectra could not be characterized because they were found to contain background peaks. Other peaks were found to contain hydrocarbons.

The total ion chromatogram (TIC) obtained for AMF-I fraction is shown in Figure 33. The chromatogram shows several peaks of separated components. This fraction was a complex mixture of compounds and appeared to contain condensed aromatic and saturated acids. The separation of this fraction was not good and mass spectra of each peak in the TIC contained fragments from other components, thus making the mass spectral identification difficult. Two nitrogen compounds were, however, identified in this fraction from their mass spectral fragmentation and comparison of the spectra with spectra of pure compounds. These compounds mostly belong to pyridine type. The compounds characterized are 5,7-dimethyl-octahydro-indolizine (122), and Benzoquinoline/Benzoisoquinoline (468,545). The mass spectra obtained are reproduced in Figures 33a through 33c along with mass spectra of pure compounds. In this fraction, the base compound with mass number 179 was identified at two different scan numbers. These two mass spectra are almost similar. There are eight possible isomers for the base compound of mass 179 which have similar spectra. This is because substitution of one carbon atom by a nitrogen atom results in three isomers in the case of anthracene(i.e. Acridine, benzo[g]quinoline and benzo[g]isoquinoline) and five isomers in the



AHF-III SCAN NUMBER 547

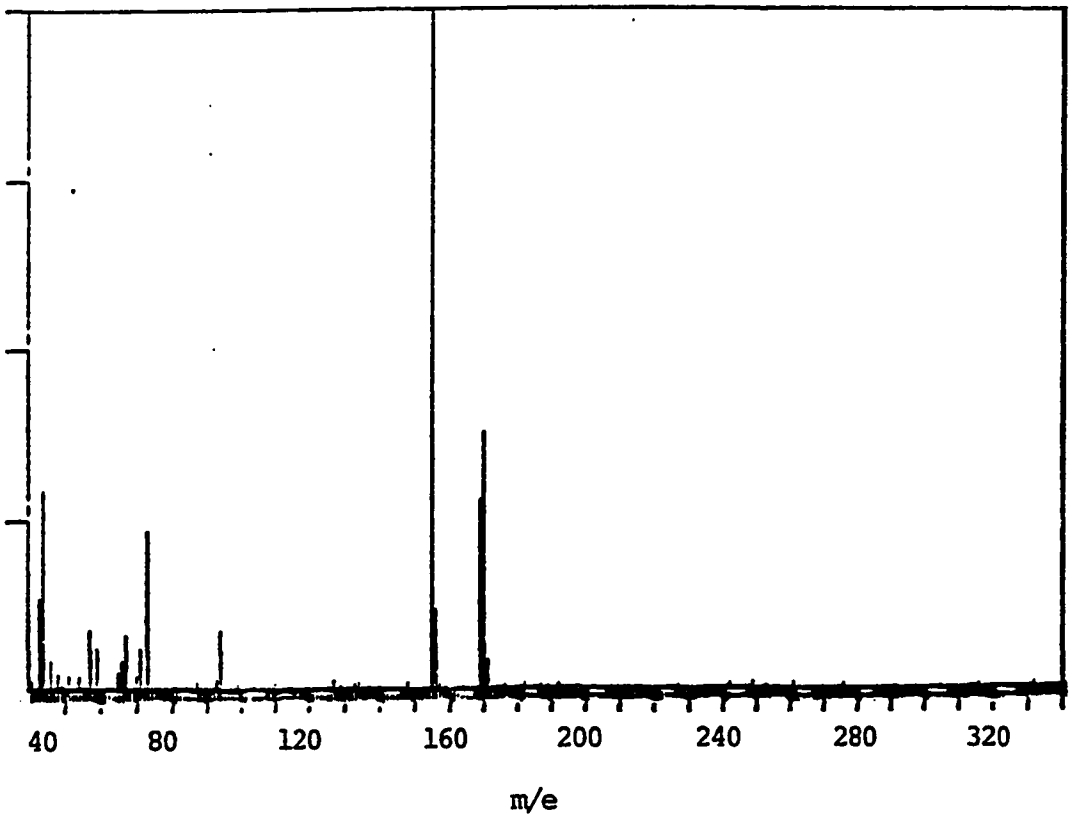
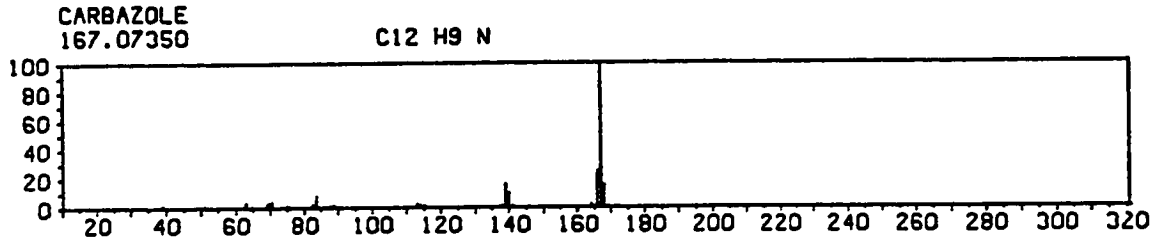


Figure 32a. Mass Spectrum of a Component obtained from AHF-III Fraction compared with Mass Spectrum of pure 1-Cyanoisoquinoline 2-Oxide



AHF-III SCAN NUMBER 1372

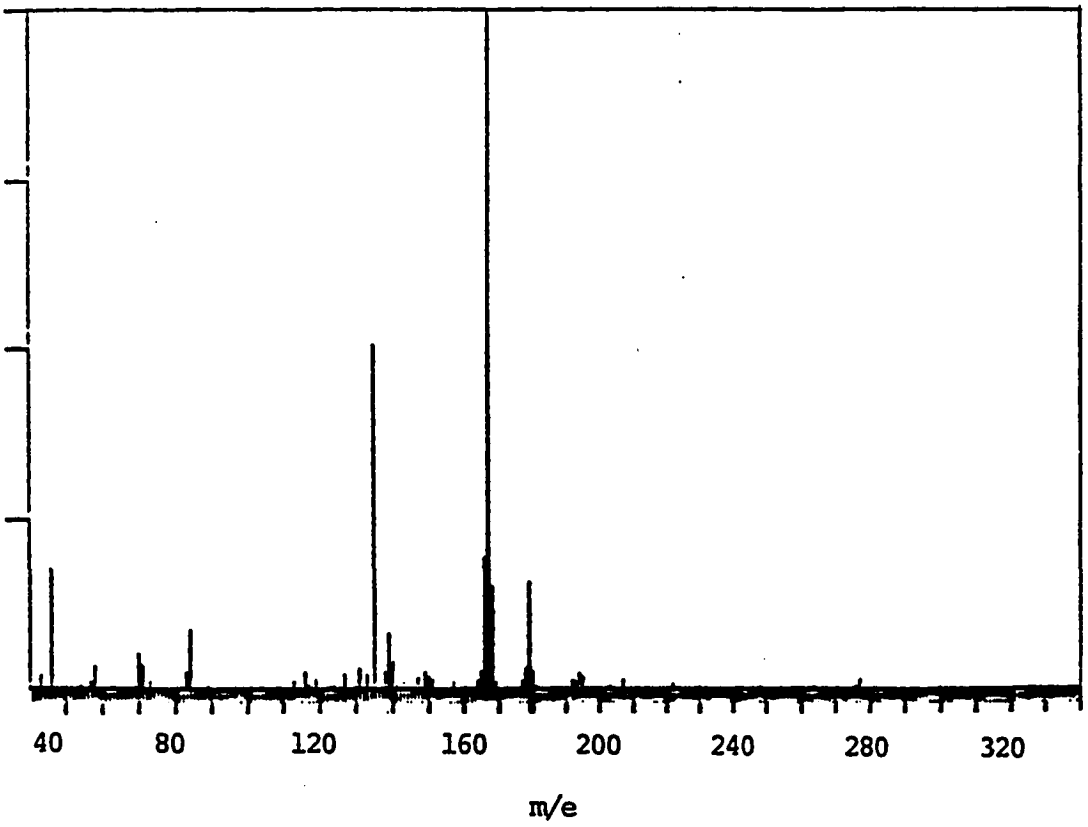


Figure 32b. Mass Spectrum of a Component obtained from AHF-III Fraction compared with Mass Spectrum of pure Carbazole

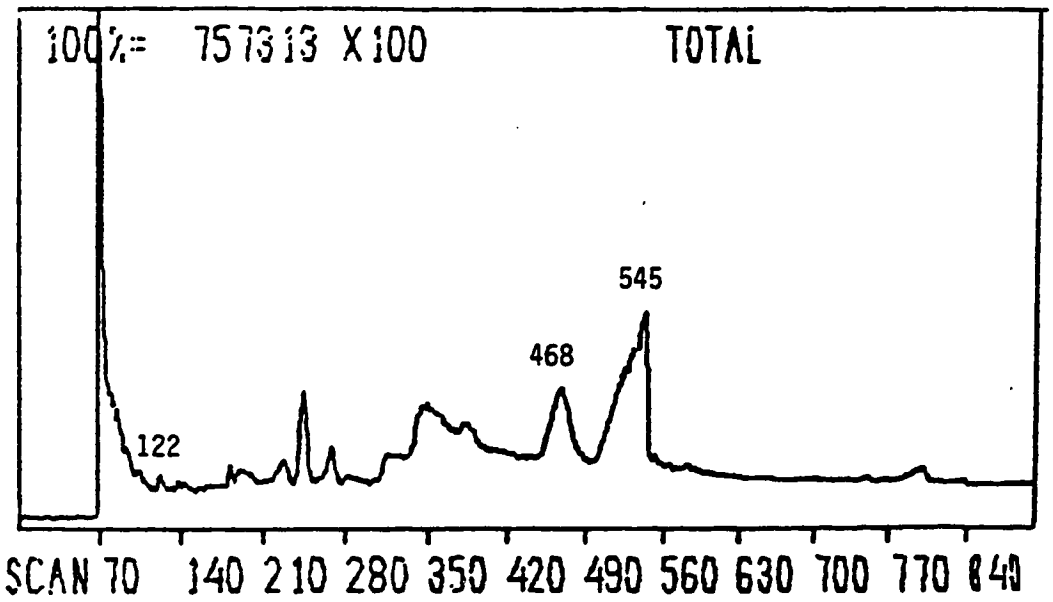
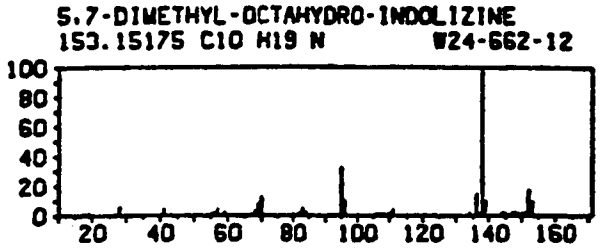


Figure 33. Total Ion Chromatogram of AMF-I Fraction



AMF-I SCAN NUMBER 122

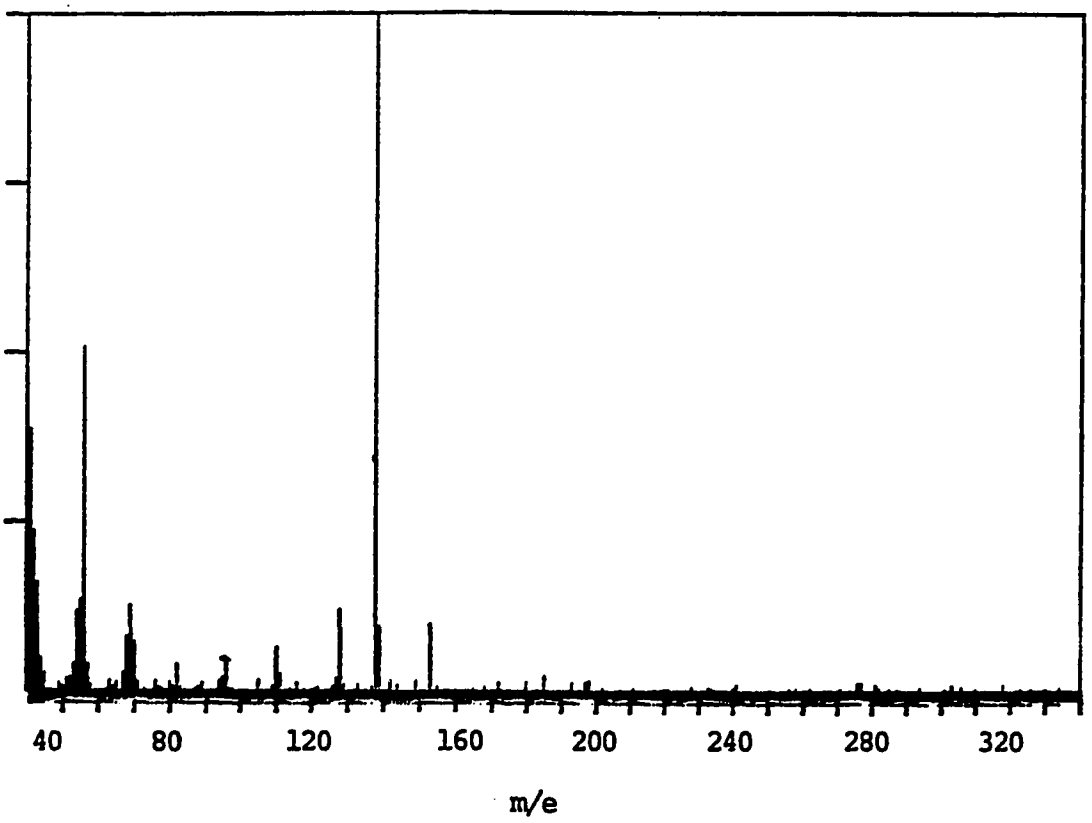


Figure 33a. Mass Spectrum of a Component obtained from AMF-I Fraction compared with Mass Spectrum of pure 5,7-Dimethyloctahydro Indolizine

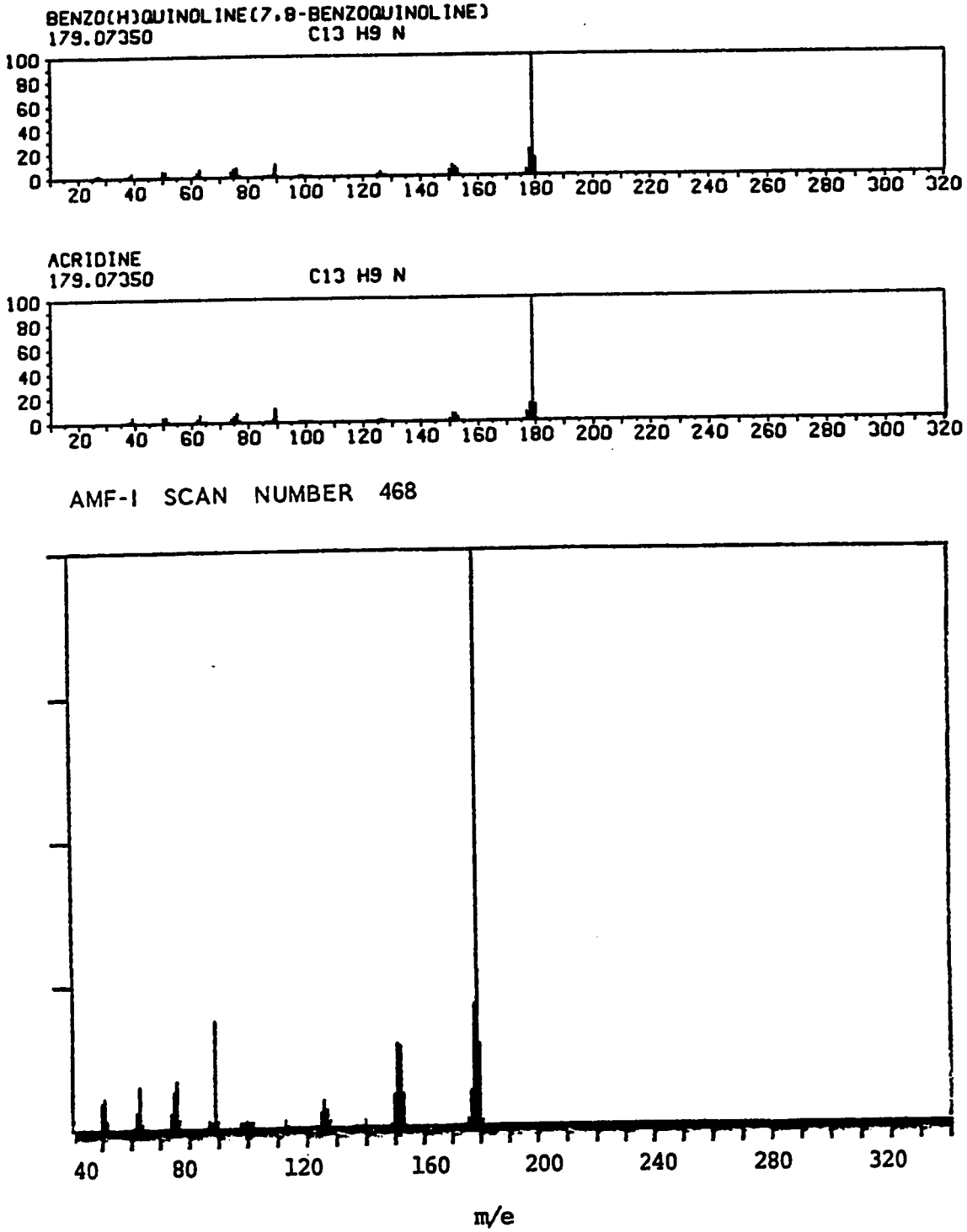
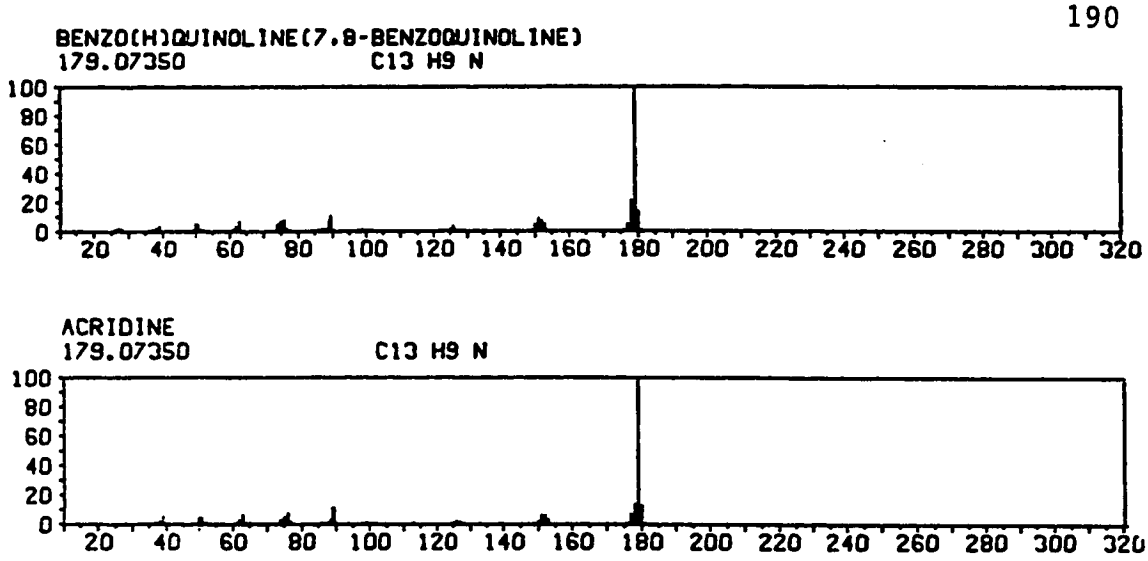


Figure 33b. Mass Spectrum of a Component obtained from AMF-I Fraction compared with Mass Spectra of pure Acridine and 7,8-Benzoquinoline



AMF-I SCAN NUMBER 545

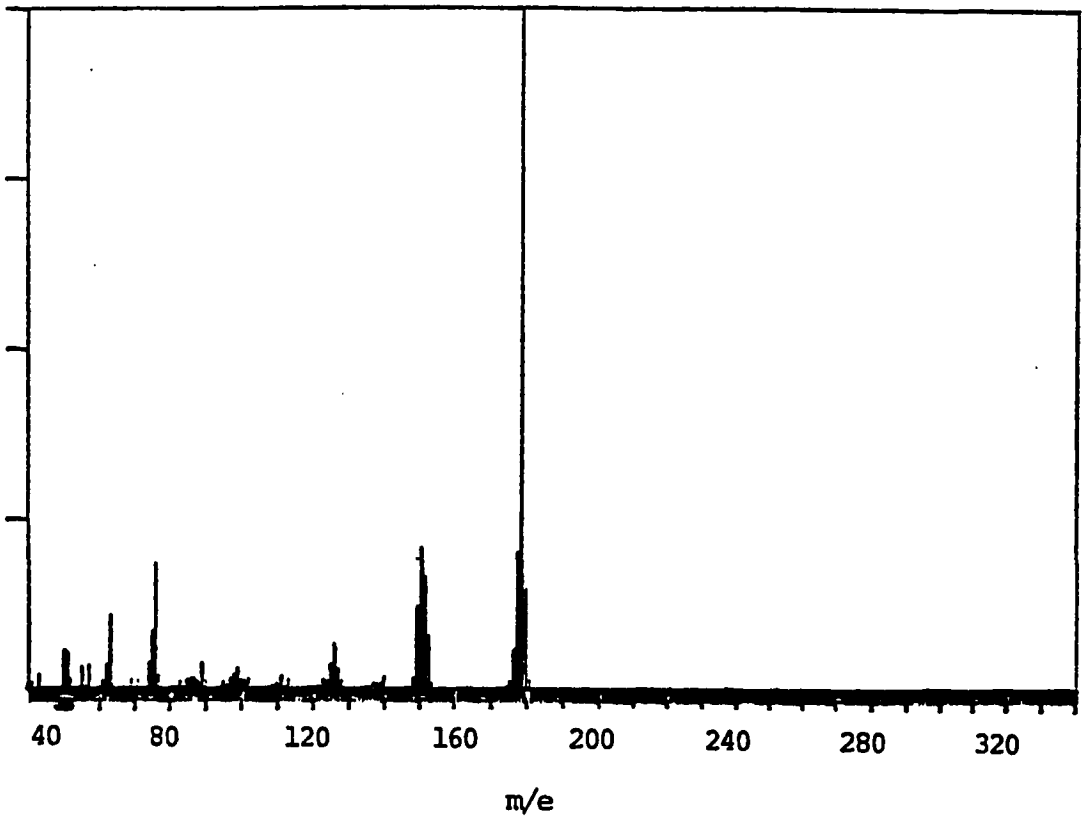


Figure 33c. Mass Spectrum of a Component obtained from AMF-I Fraction compared with Mass Spectra of pure Acridine and 7,8-Benzoquinoline

case of phenanthrene (benzo[f]quinoline, benzo[h]quinoline, benzo[f]isoquinoline, benzo[h]isoquinoline and phenanthridine). The mass spectra of other components which appeared in the total ion chromatogram (TIC) of this fraction contain the characteristic homolog ion series of phenylalkane (77,91,105,119,133,147,.....) and carboxylic acids. Moreover, these spectra appeared to contain more than one component and could not be characterized.

The total ion chromatogram (TIC) obtained for AMF-II fraction is shown in Figure 34. The chromatogram shows a number of peaks of separated components which are at lower scan number compared to other fractions. Three nitrogen compounds were identified in this fraction from their mass spectra. These compounds are N-N-butylpyrrole, 2,6-dimethylaminopyrimidine and isobutyramide at scan numbers 81, 101 and 110 respectively. These compounds are of low molecular weight as compared to compounds identified in its Arab Heavy counterpart. The mass spectra obtained are reproduced in Figures 34a through 34c along with mass spectra of pure compounds.

The total ion chromatogram (TIC) obtained for AMF-III fraction is shown in Figure 35. The chromatogram shows a number of peaks of components at lower scan number compared to its Arab Heavy counterpart AHF-III. Two nitrogen compounds were identified in this fraction from their mass spectra which are of amide type. These compounds are N-phenyldiacetamide (463) and caffeine (1372). The mass spectra obtained are given in Figures 35a and 35b respectively along with mass spectra of pure compounds. Caffeine has not been reported yet in petroleum and its fractions but the mass spectra obtained strongly advocates its presence in this fraction.

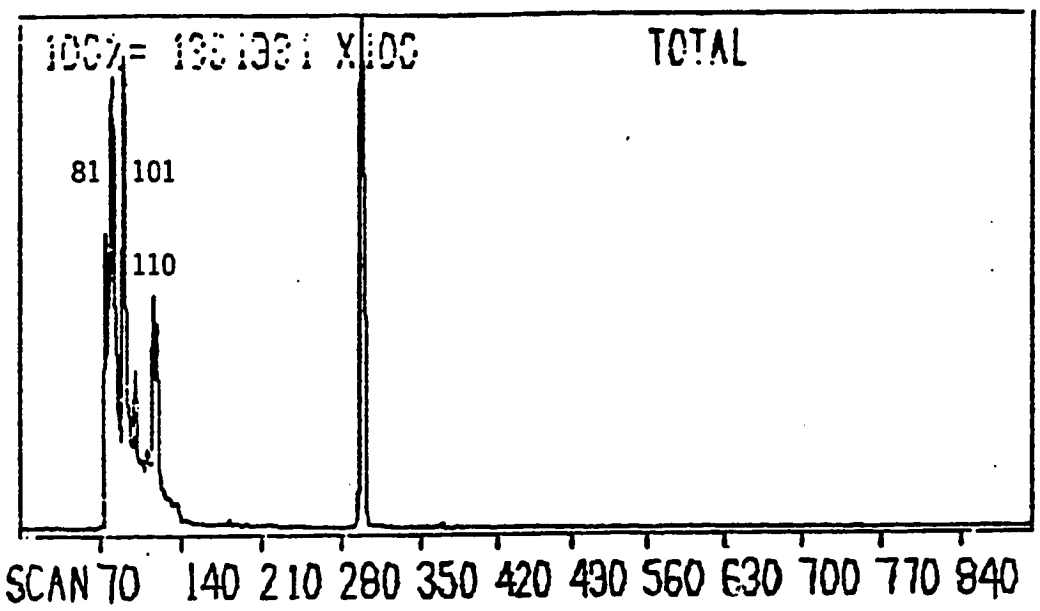
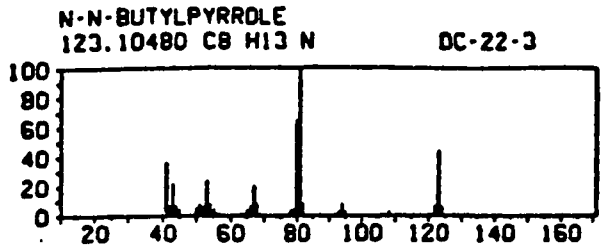


Figure 34. Total Ion Chromatogram of AMF-II Fraction



AMF-II SCAN NUMBER 81

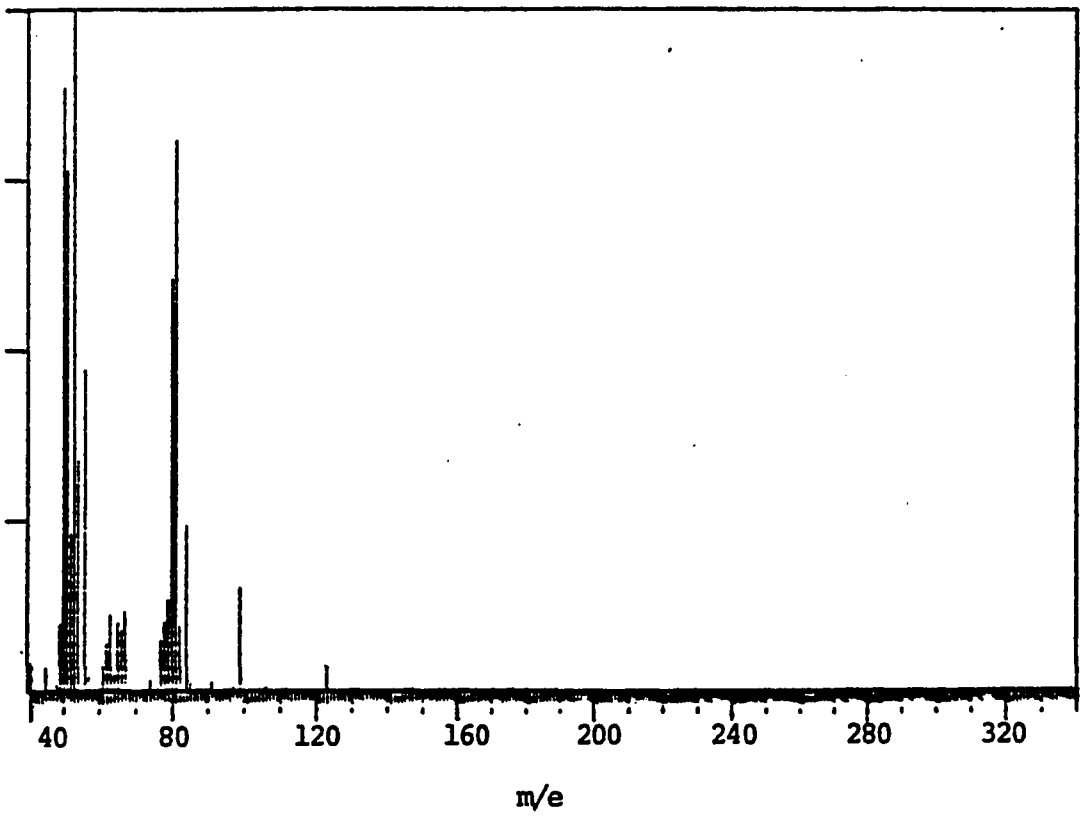
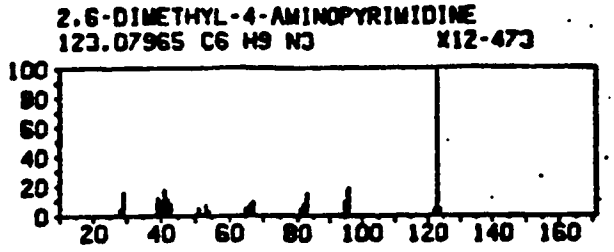


Figure 34a. Mass Spectrum of a Component obtained from AMF-II Fraction compared with Mass Spectrum of pure N-N-ButylPyrrole



AMF-II SCAN NUMBER 101

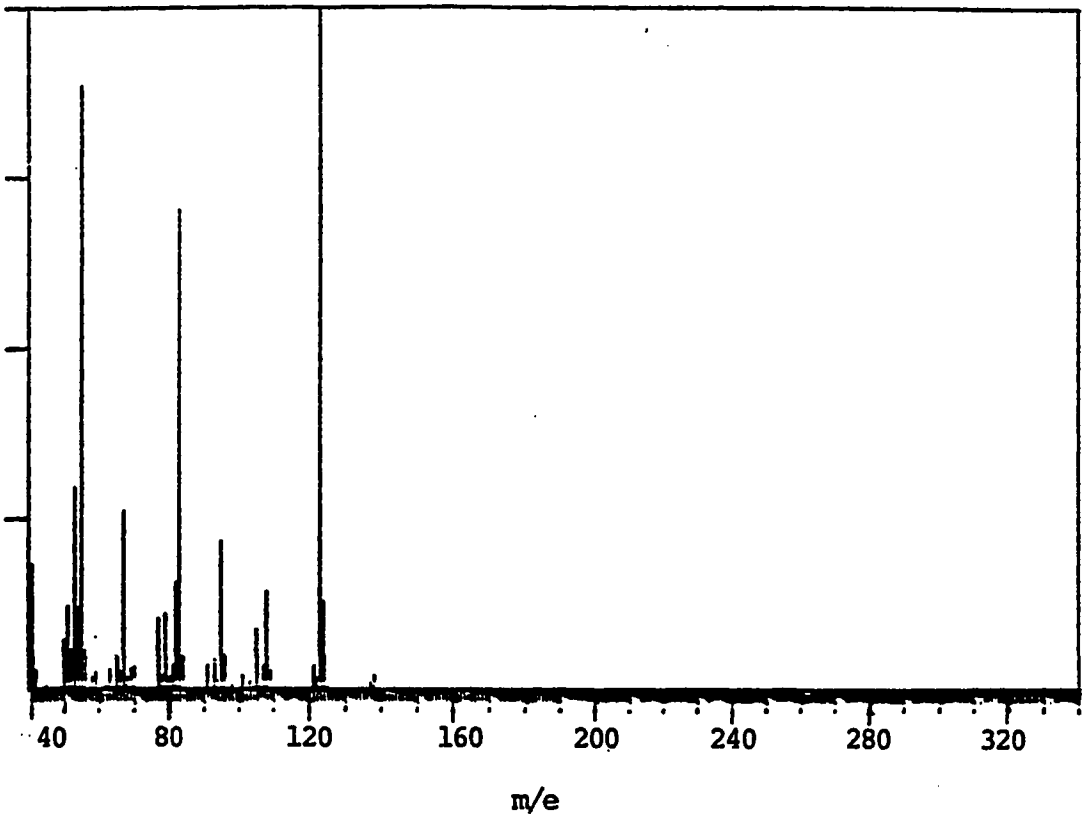
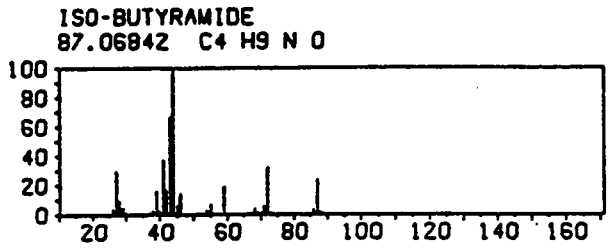


Figure 34b. Mass Spectrum of a Component obtained from AMF-II Fraction compared with Mass Spectrum of pure 2,6-Dimethyl-4-Aminopyrimidine



AMF-II SCAN NUMBER 110

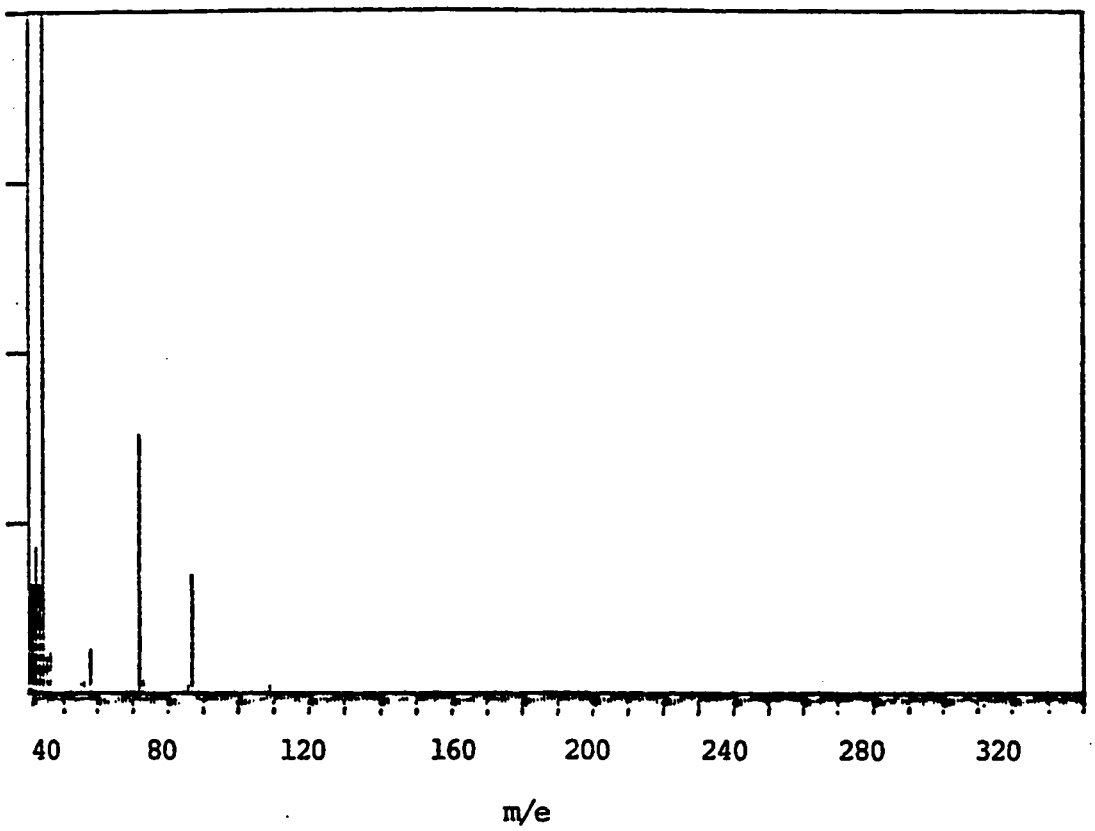


Figure 34c. Mass Spectrum of a Component obtained from AMF-II Fraction compared with Mass Spectrum of pure Isobutyramide

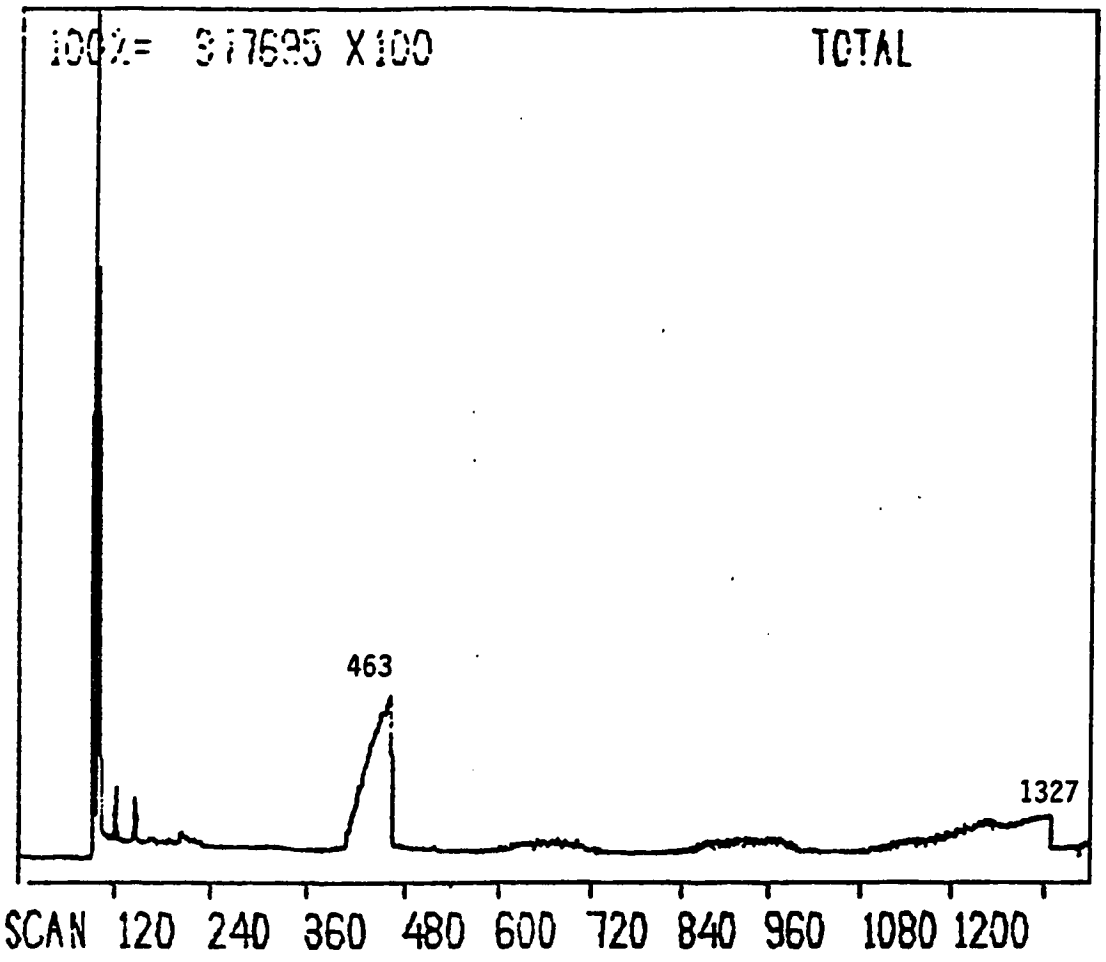
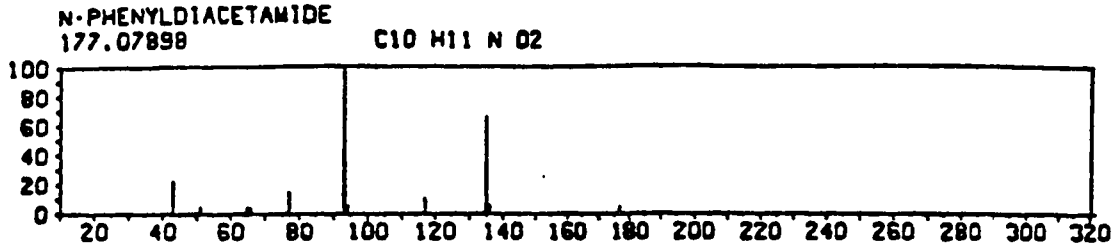


Figure 35. Total Ion Chromatogram of AMF-III Fraction



AMF-III SCAN NUMBER 463

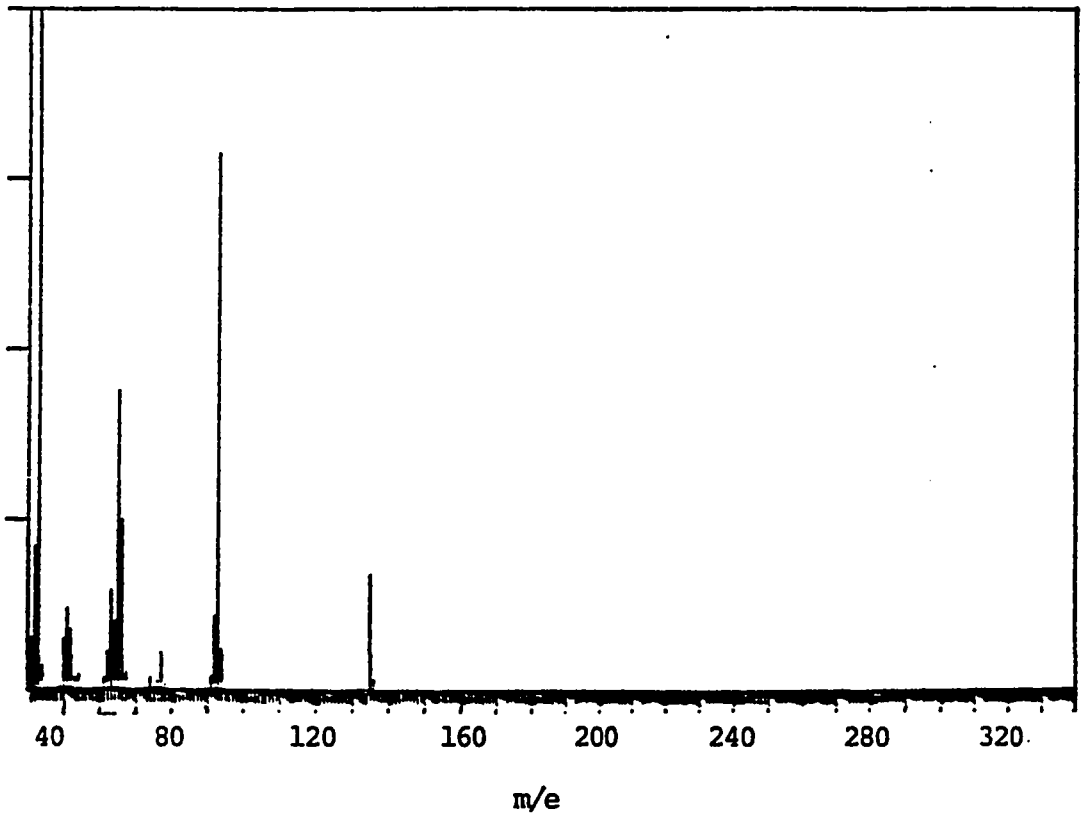
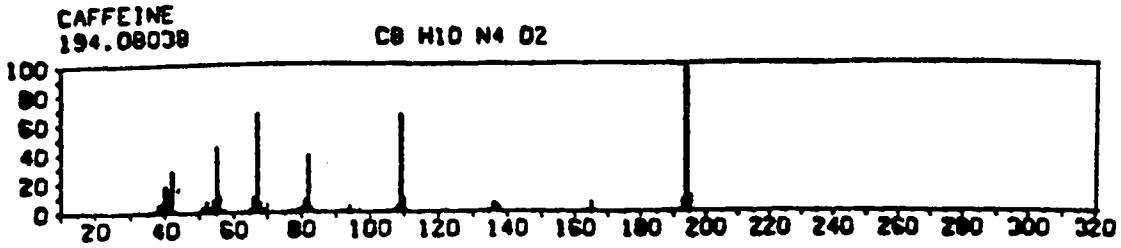


Figure 35a. Mass Spectrum of a Component obtained from AMF-III Fraction compared with Mass Spectrum of pure N-Phenyldiacetamide



AMF-III SCAN NUMBER 1327

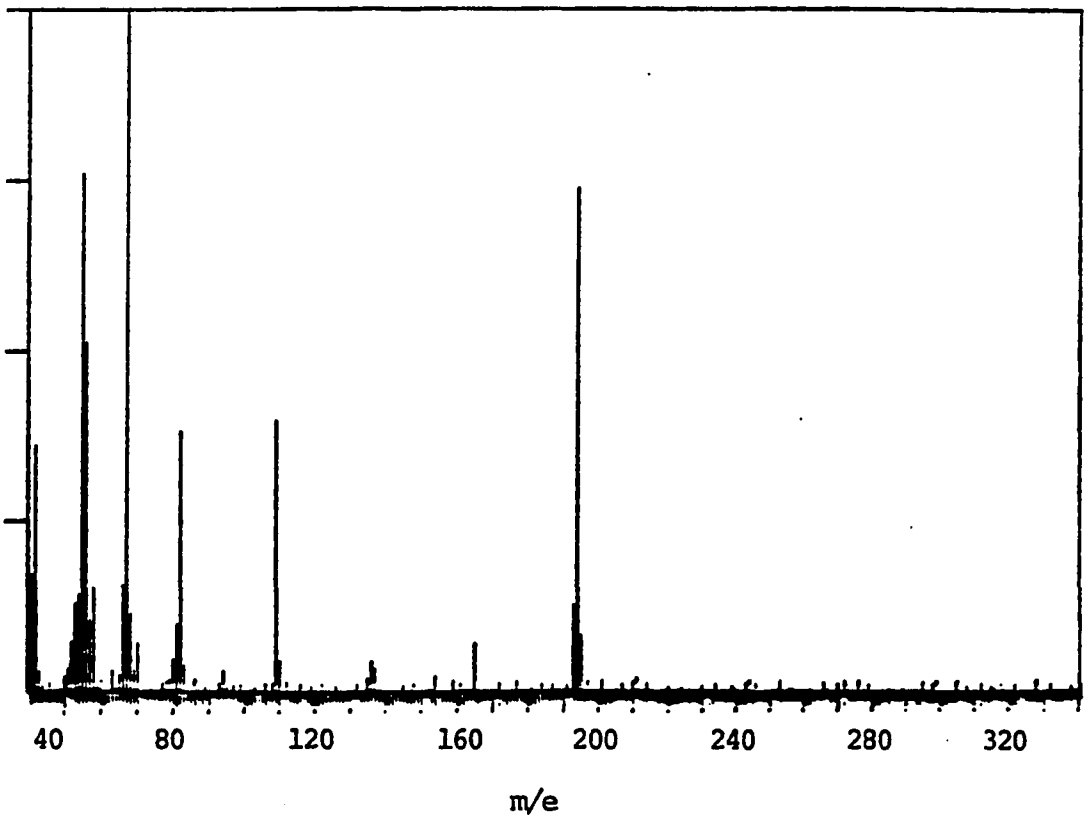


Figure 35b. Mass Spectrum of a Component obtained from AMF-III Fraction compared with Mass Spectrum of pure Caffeine

CONCLUSIONS

1. The experimental results have shown that Saudi Arabian crude oils have varying amount of heteroatomic contents such as nitrogen and sulfur and there is a gradual decrease from Arab Heavy to Arab Berri through Arab Medium and Arab Light crude oils. The gravity, viscosity and pour point of these crude oils indicated that percentage of high molecular weight components are more in Arab Heavy as compared to other crudes and decrease with increasing API gravity.

2. The elemental analysis of all four high-boiling distillates has shown that the aromaticity, heteroatomic contents, polarity and degree of condensation decrease from Arab Heavy to Arab Berri through Arab Medium and Arab Light distillates. This decrease is in accordance with a decrease in weight percent carbon, nitrogen, sulphur and oxygen and an increase in weight percent hydrogen, API gravity and weight percent yield on crude.

3. The average molecular weights of distillates decrease from Arab Heavy to Arab Berri. The Arab Medium and Arab Light distillates lie in Between. This decrease in average molecular weight is accompanied with an increase in API gravity of these distillates.

4. The nonaqueous potentiometric titration data indicated that there is a gradual decrease in basicity of these distillates with a decrease in the total nitrogen contents. Generally, all distillates contained fairly low amount of basic nitrogen compounds.

5. Separation of distillates into different classes of compounds has

shown that Arab Heavy distillate contains relatively higher amount of acids, bases and neutral nitrogen compounds as compared to Arab Medium distillate and the amount of these polar compounds decreases with a decrease in the total nitrogen present. The total nitrogen compounds were, however, very low.

6. Infrared spectroscopy can be used for the qualitative and quantitative determination of different compound types present in the polar fractions of high-boiling distillates.

7. Nonaqueous potentiometric titration can be employed for the quantitative determination of compound types present in the polar fractions of high-boiling distillates.

8. Quantitative determination of compound types in polar fractions by infrared analysis can be compared to the similar data produced by nonaqueous potentiometric titration of these samples.

9. The gas chromatographic analysis of HPLC fractions has shown that the polar material was effectively separated into pyridine, pyrrole and amide type compounds. Eleven nitrogen compounds belonging to three compound types were tentatively identified from their retention times.

10. Sixteen nitrogen compounds in the six HPLC fractions obtained from Arab Heavy and Arab Medium nitrogen concentrates were positively identified by GC-MS analysis. These compounds represent three different classes of nitrogen compounds namely pyridines, pyrroles and amides.

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